FACTORS AFFECTING THE SOLUBILITY OF OXYGEN IN MOLTEN IRON IN EQUILIBRIUM WITH FeO-MnO-SiO_2 SLAGS.

by

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S Y N O P S I S.

Previous work on the equilibrium between iron containing oxygen and molten ferrous slags has been largely concerned with pure FeO-MnO slags and silica saturated slags. Even in these limited fields complete agreement on the equilibria has not been attained. The present work was carried out to obtain further information on the above equilibria and to extend investigations to slags not saturated with silica.

Iron was melted in a purified nitrogen atmosphere in slip cast magnesia crucibles under various iron-manganese-silicate slags at 1550°, 1575° and 1600°C for times varying from 45 minutes to 2 hours after which samples of slag and metal were taken. The equilibrium was approached from both sides in different experiments. Slag samples were analysed for FeO, Fe_2O_3, MnO, MgO and SiO_2, and metal samples for Manganese, silicon and oxygen.

The solubility of oxygen in iron under a pure iron-oxide slag increased from 0.19% at 1550°C to 0.22% at 1600°C. The variation of

$$K_{Mn} = \frac{(MnO)}{(FeO).[\%Mn]}$$

with temperature was given by the following expression:

$$\text{Log } K_{Mn} = \frac{7250}{T} - 3.356$$

The mean values of the corresponding constants for silica saturated slags were found to be 15.95 and 13.3 at 1550°C and 1600°C respectively compared with 15.5 and 11.7 given previously by Körber and Oelsen(1). A value of -6000 cals. for the free energy of formation of rhodonite from manganese-oxide (liquid) and silica at 1600°C was derived from the above data.

The mean activity coefficients of FeO and MnO in silica saturated FeO-MnO-SiO_2 slags were found to be 0.94 and 0.23 respectively at 1600°C When combined with the data of the other workers, the results indicate that γ_{MnO} rises with increasing temperature.

$K'_{Si} = [\%Si][\%O]^2$ was found to be 2.9×10^{-5} which is in good agreement with most previous work.

The results obtained in equilibria with slags not saturated with silica were used to derive iso-oxygen solubility (in metal) curves and ferrous oxide iso-activity curves for FeO-(MnO, MgO)-SiO_2 slags at 1600°C. A small positive deviation from ideality was observed, the greatest deviation being along the FeO-Mn_2SiO_4 join. Curves were also constructed showing the manganese and silicon contents of metal in equilibrium with FeO-(MnO,MgO)-SiO_2 slags at 1600°C. The manganese contents did not compare favourably with those of Turkdogan and Pearson(2).

Calculations were made of the activities of MnO and SiO_2 in MnO-SiO_2 slags at 1600°C and the results obtained were used to derive free energies of formation of MnO-SiO_2 slags at 1600°C and the chemical potentials of the component oxides.

A comparison of values of K'Si obtained with slags not saturated with SiO_2 with those obtained with silica saturated slags showed discrepancies which suggested that silicon and oxygen affected each other's activities. An alternative explanation was that molten metal was able to reach equilibrium with the silica sampling rod during the 1-2 seconds of sampling.

The results obtained were used to derive the relationship between the amount of a manganese-silicon deoxidiser suitable for the formation of liquid deoxidation products, the percentage of oxygen removed and the final oxygen contents of molten iron at 1600°C. Curves were also obtained showing the ideal manganese-silicon ratio in the deoxidiser and the final oxygen content of the iron for various initial oxygen contents. The ideal ratio varied between 3 and 6 for most normal practical requirements but fell rapidly when high degrees of deoxidation were required.

A number of experiments were carried out in which about 1% of manganese-silicon deoxidiser was added to about 50 gms. of molten iron containing oxygen and samples taken at varying times after the deoxidiser addition. In all cases the residual oxygen contents were higher than those predicted from the equilibrium experiments and it was apparent that even after 1 minute, rapid transfer of oxygen from slag to metal was taking place.

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Recent Developments in Core & Mould Making Processes.

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INTRODUCTION.

In the space of a brief review it would be impossible to discuss fully all the important developments which have taken place in foundry practice in recent years. This paper has, therefore, been restricted to cover the latest developments in core and mould making processes, which play a major part in foundry practice and control to a large extent the rate of production and the quality of castings, especially such features as porosity, surface finish and dimensional accuracy.

Until recently cores and moulds have generally been made from oil bonded sands. Loam compounds incorporating drying oils, molasses, etc., have also been used as binders but the rate of industrial production has increased considerably and conventional oil—or loam—sand practices of core and mould making, although still in use in more than 80 per cent. of all foundries, have not proved adaptable to high production rates. For modern requirements, it is necessary to obtain increased production by maximum utilisation of the available manpower and working space on the one hand and by reducing time and physical effort on the other. Amongst the new core and mould making processes, utilising sand as the basic material, the "C," "D" and CO_2 processes have established themselves as suitable production processes. Their applicability depends on economic considerations and on individual factors which vary from foundry to foundry. In this review the above mentioned processes are discussed and the probable extent of their future use is outlined.

"C" and "D" PROCESSES.

GENERAL.

Both these processes are used in the field of small precision castings only. The "C" process utilises a powdered resin/sand mixture and a hot pattern to make cores or moulds. Powdered resin in the resin/sand mixture in contact with the hot pattern softens and binds the sand round the pattern. When the desired thickness has been obtained, the mould, along with the pattern, is sent to oven for a short time baking. After baking, the mould is stripped off the pattern. Two such half-moulds, produced in this way, are fastened together to give a complete mould.

The "D" process, however, utilises a special core oil as the binder with sand. The special oil/sand mixture is blown from a sand blower into the space between a cold pattern and a hot contour plate. The moulds, formed, are stripped out from the pattern and sent for baking into the oven. Due to certain practical difficulties in the process, which will be discussed later, liquid resin/sand mixture and hot patterns have been used in this process recently. Besides powdered and liquid resin, used in the "C" and "D" processes respectively, the properties of the different types of sand and additions also influence markedly the properties of moulds and cores.

SAND.

Sand with an A.F.S. number of 75-230 and a clay content preferably nil but in any case below 2 per cent. is used as the basic material. Any grain shape may be used provided it is dry and free from easily fusible metallic oxides. Much less sand is used than in conventional oil-sand practice, so that the higher cost of the sand is largely offset. Admixture of 20-30 per cent. sand with an A.F.S. number of 40-60 gives better permeability and a good shell strength without impairing the quality of the castings. The author

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found that such a mixture gave very satisfactory results especially with alloyed cast iron. Wherever the pouring temperature exceeds 1,300° C., it is desirable to add some coarser sand to obtain a good finish.

BINDER.

The binder in the " C " process may be either a single or two stage phenolic resin. Two stage phenol formaldehydes give better storage properties and shell life. An accelerator, usually finely powdered hexamethylenetetramine, is used with the two-stage resins to complete the hardening reaction while hot. The amount of binder used depends on the fineness and quality of the sand. Generally, within the above mentioned sand range, 5—8 per cent. binder has been found to give the best results. The amount of accelerator used is 10—15 per cent. of the binder.

Resins other than phenol formaldehyde (cf. urea and melamine formaldehyde) appear to be inferior with regard to ease of stripping, glaze, smoothness, strength, flowability and mature dropping. Further investigations are proceeding on the ability of other additions such as suitable clays (e.g., bentonite, montmorillonite etc.) to reduce resin consumption without affecting shell strength and other desirable properties, the use of inhibitors for use with non-ferrous castings, and of plumbago to improve surface finish.

In the " D " process using a cold pattern a special process oil was initially used as a binder. Addition of 2—2·5 per cent. was reported to give a satisfactory blowability value. Results obtained by the author, with available patent oils, such as Permol, Glycol, etc., and also with pure linseed oil binders, under ' D " process conditions, were not very satisfactory when compared with conventional oil-sand practice. Oil when used alone as a binder presents certain practical difficulties because its viscosity is lower at high temperatures and as a result sand loosening occurs. Unless they are fully baked as in conventional oil-sand practice, oil-bonded cores are very weak while hot, especially in the " D " process where within the range of 200-250° C., the mould (heated by contact with the hot contour plate) is to be stripped from the cold pattern within a reasonable time, for further baking or curing. This weakness may be a major factor in shell distortion and resultant dimensional inaccuracy. Furthermore, the oil film formed on the core box and pattern plates from the oil bonded sand leads to stickiness and gives rise to difficulties in smooth stripping. These difficulties have been partly overcome by introducing such materials as powdered hydrocarbons, iron-oxide, fly-ash etc., which act as a filler and drying material in the oil compound at elevated temperatures. Addition of these " extenders " varies from 0·5 per cent. of the sand weight in the case of hydrocarbons to 1 - 2 per cent. and 6 per cent. in the case of iron oxide and fly-ash respectively.

Because of the difficulties associated with the use of oil in the " D " process, liquid phenolic type resins have been developed recently as an alternative. A hot pattern is used with these binders, and to avoid stickiness, a little light distillate oil is used. Hot contour plates and cold patterns may also be used but the use of hot patterns is becoming popular because of its ease of working.

EQUIPMENT REQUIRED.

In both the " C " and " D " processes, where the dimensional accuracy required in the castings is ± 0·005 ins., accurately dimensioned smooth patterns are essential, of uniform section and a thickness sufficient to maintain an adequate temperature head for the desired shell formation. Metal patterns are suitable for both processes. The metal used should not distort at elevated temperatures and should have a coefficient of thermal expansion which

does not offset the dimensional accuracy of the shells made on the pattern. Brass, cast iron and aluminium, are used, although the latter is the least suitable due to its high linear expansion (approximately twice those of brass and cast iron) and thermal conductivity (approximately 25 and 4 times higher than brass and cast iron respectively). However, aluminium can be used when thick patterns are required for certain castings in the " C " process, provided proper allowance is made for expansion. They may also be used in the " D " process without any trouble, when working with cold pattern. Cast iron patterns give the most satisfactory results in both processes but are heavy in handling and expensive.

To facilitate working, mounting plates are necessary in both processes. The " D " process also requires contour plates, preferably with a large number of blowing holes. Stripping pins and ejector plates may also be necessary in both processes for smooth removal of the shell from the pattern. Their use mainly depends on the design of the castings.

MIXER & MIXING PRINCIPLES.

When resin is used as a binder, the conventional oil - sand mixer does not give thorough mixing, and defects, known as resin spots occur in the finished castings arising from the presence of localised lumps of resin in the mix. For efficient mixing and binding, powdered resin having an A.F.S. number ranging from 120 to 140 is in general use in the " C " process. As such a fine resin absorbs moisture readily and tends to form lumps, it should not be allowed to remain exposed to the atmosphere for long periods. Therefore a closed type rotating tumbling mixer is preferable. Addition of a small percentage of liquid resin, paraffin or lubricating oil to the sand before adding the powdered resin prevents dust and gives a uniform resin/sand mixture which does not pick up moisture during storing. The rotating tumbling mixer can also be used when working with liquid resin in the ' D " process as well as any conventional oil/sand mixer. In both processes milling time varies from 8 — 10 minutes and sand, direct from the drier, should not be used unless its temperature does not exceed 50 — 60° C., as mixing at a higher temperature leads to stickiness in the mixer. In the " C " process addition of 7·5 — 10 per cent. of zircon flour to the resin/sand mixture used for medium carbon and stainless steel castings has been reported to improve surface quality. Zircon flour additions to a base sand of A.F.S. number 230 containing 10 — 10·5 per cent. resin undoubtedly improves the surface finish of such castings and decreases metal penetration, but they also increase costs due to the extra resin consumption resulting from the zircon addition and to the extra cost of the zircon flour. During some recent trial experiments on mild steel castings the author obtained very satisfactory results with a 7 per cent. resin/sand mixture, simply by adding 40 per cent. of coarse sand (A.F.S. number 30 — 80) and treating the mould face with plumbago.

The proportion of resin to sand varies from foundry to foundry depending on the thickness and temperature of the castings. For small castings ($\frac{1}{2}$—10 lb.) made of cast iron or any non-ferrous material, 5 — 6 per cent. resin will be sufficient, using sand of A.F.S. number 150 — 230 with a 30 — 40 per cent addition of coarser sand of A.F.S. number 90 — 120, if required. For heavier castings, weighing from 15 — 30 lb., and for all castings, when the pouring temperature is high, 7 — 7·5 per cent. resin gives good results with a mixture of fine sand (A.F.S. number 150—230) with 30 — 40 per cent. coarser sand (A.F.S. number 30 — 80). Patent resins like " Resolite," " Cellobond " etc., may be used.

In the " D " process, 2 — 3 per cent.

liquid resin gives satisfactory results. These liquid resins are much cheaper than the powdered resins used in the "C" process. As in the latter process, coarser sand may be added to obtain improved strength and permeability.

PARTING AGENTS.

With a cold pattern, as in the "D" process, if a green strength of 0·5 — 0·7 lbs./sq. in. is obtained with an oil bonded sand containing extenders, generally no parting agent is necessary to remove the shells. But as has been mentioned, oil bonded sand gives an oil film, especially on intricate patterns and core-boxes. These are kept clean by means of a mixture of linseed oil and water.

Moulds formed on hot patterns, which are required with the powdered and liquid resins used in the "C" and "D" processes respectively, are very difficult to strip-off. Therefore before the pouring or blowing of the investment (sand/resin mixture) the metal pattern should be treated with a stripping agent to facilitate smooth parting of the shells without any distortion. Polytetrafluorethylene (P.T.F.E.) gives the best result in terms of ease of stripping and the number of moulds made per application of the parting agent, but its application to the pattern surface and subsequent removal is difficult and tedious and it is also in short supply. A solution of 4 to 5 parts by volume of silicone emulsion in 100 parts of water or white spirit when sprayed on the hot face of the patterns, gives a satisfactory result. Certain other parting agents e.g., paraffin, wax, butyl stearate, although giving good results, cause staining on the valuable pattern and also produce dense fumes due to decomposition at the working temperature.

PATTERN TEMPERATURE AND BAKING.

Pattern temperature should be controlled to give a compact thick shell on the smooth surface of the treated pattern within a reasonable time. Although the temperature range recommended for patterns varies from 175—300° C., the actual temperature will be decided by the design of the casting and the resin/sand mixture. A straight pattern of uniform thickness gives no trouble. Difficulty is experienced when heavy and thin sections are present in the same casting, as the shell in heavier sections may be overcured, whereas that in the thin sections remain undercured. It has been generally agreed that a pattern temperature of 200—215° C. with an oven temperature ranging from 300—315° C. is suitable for most work.

When patterns are simple and uniform in section, higher pattern temperature may be used. This will produce a thicker shell within a very short time. With pattern temperature of 200—215° C., a contact time of 10—12 seconds in the "C" process will build up a shell ranging from $\frac{3}{16}$" to about $\frac{1}{2}$" in thickness. Shells thus produced are sent to the ovens for curing or hardening. The curing time varies from 1—4 minutes, depending on the shell thickness and the oven temperature. Undercuring of shells leads to dimensional instability and physical tests on standard samples should be carried out regularly for each batch, e.g., compression, tensile and flexural strength tests for which conventional sand testing methods are adequate. With properly hardened moulds or cores, the compression strength varies from 1,150—2,500 lbs./sq. in. and the tensile strength from 250—450 lbs./sq. in. The actual values depend on the quality and per cent. of binder used, as well as on proper curing and to some extent on the type and range of sand used.

In the "D" process, using liquid phenolic resins with hot patterns and cold contour plates, the shell formed is ejected by the stripping pins or plates and sent to the hardening ovens, where the temperature range is the same as in the

" C " process. However, curing time is longer, increasing from 5 to 15 mins. as the oven temperature decreases from 320° to 240° C., for a 0·5 inch thick shell. During some trial experiments, the author used hot pattern and contour plates with a liquid resin/sand mixture of good blowability value, and obtained satisfactory shells which could be handled quickly without any distortion. If the pattern and contour plate temperatures are kept above 200° C., then within 2—3 minutes after blowing, the shell acquires good compactness on both surfaces. In this way curing time can be brought down to a minimum. The only difficulty experienced is that contour plates require frequent treatment to remove adhering particles in the blowing holes and edges.

When special " D " oil is used as a binder, the shells formed have a green strength of 0·5—0·7 lb./sq. in. Careful handling is necessary to avoid distortion. The shells are baked in thermostatically controlled ovens or in any conventional type of oven provided the required temperature can be maintained. A properly baked " D " process shell would give more than 300 lb./sq. in. in tensile strength on an A.F.S. tensile specimen with a dry hardness varying from 90—95 plus.

MOULD AND CORE MAKING MECHANISM.

In the " C " process, mould formation can easily be carried out with a top-face open box or as it is generally called, an " inverting box," which can easily be inverted by gearing or by a lever system. The hot pattern mounted on a pattern plate is fitted in an inverted position on the open face. When the box is inverted, the investment falls on the treated hot pattern. The thermo-setting properties of the resin form a plastic bond in the sand, and the mould forms on the pattern surface. The time of contact depends on the pattern design and temperature and the required shell thickness. For core-making, a blowing machine can be used but the dumping technique, as mentioned above, is more economical.

In the " D " process, a core blowing machine giving an air pressure of 80—100 lb./sq. in. is necessary, whether a cold pattern and a special oil/sand mixture or a hot pattern and a liquid phenolic resin bonded sand is used. A core blower with a lower air pressure may be used but in such a case, the number of blowing holes in the contour plate should be increased, otherwise a uniform, dense and compact mould or core may not be obtained. The thickness of a shell formed by this process will depend on the space left between the pattern and contour plate.

DISCUSSION.

Both processes are used for precision castings only. The maximum casting weight in general is 30 lb. due to the limitation imposed by shell thickness. Properly backed moulds, however, can produce castings weighing more than 2 cwt., although backing is an extra operation which costs money and takes time. Either metal strengtheners or recovered foundry sand may be used for backing.

By using either the " C " or " D " process, castings may be obtained with a good surface finish and dimensional tolerance and therefore further machining may be avoided, thereby decreasing considerably the cost of production. The time required to make moulds and cores is very little compared with that for conventional sand practice. In America, machines, which will produce cured and stripped moulds automatically, are already in production. The moulds can be stored for considerable periods. Metal patterns once made, can provide hundreds of castings without replacement. Compared with conventional sand practice these processes require very little floor-space, so that establishment costs are also reduced.

Application of these processes to general foundry practice where the number of castings of any one type is small and the castings may vary from ½ lb. to 20 tons, has not been very promising. Except under special circumstances where casting accuracy is vital and cost is of secondary importance, jobbing foundries cannot derive much benefit from these processes. This is mainly because accurate metal patterns are so costly that unless a large number of castings are made, the pattern price alone will put a heavy cost on the article. Furthermore, provision would need to be made for controlled heaters, sand mixers, inverting boxes, core blowers, contour plates, stripping pins, ejector plates etc., which although they cover a relatively small amount of floor-space, add to the cost of production. The methods have been successfully applied in foundries producing a large number of standard small castings up to 2 cwt. in weight. Foundries in the automobile, aircraft, bicycle, diesel engine, textile machinery, etc., industries, are most suitable for the adoption of these methods. Although the cost of basic materials may appear high, any foundry suitable for the adoption of these methods would consider the cost and quality of the finished product in relation to those of conventional sand practice.

The cost of oil or liquid resin is much lower in the "D" process than in the "C" process. On the other hand, uncured moulds or cores in the "D" process cannot be easily handled, curing time is longer and more mechanisation is required for mould and core making. Furthermore, there is not complete agreement on the best type of mechanisation for the "D" process and present equipment may very quickly become obsolete. In the "C" process, making and handling of moulds and cores is quick and easy and in spite of the higher cost of resin, higher rates of production can easily give a lower cost of production.

THE CARBON-DIOXIDE PROCESS.

GENERAL.

When clean dry sand is mixed with sodium silicate, it hardens when air-dried. Reports published before and during the war did not encourage application of the process, since the severe sintering and metal penetration which occurred made fettling impossible and led to scrapping of castings. On the other hand, certain recent publications suggest that previous objections to the use of sodium silicate may have been due to imperfect technique rather than to the process itself. The main disadvantage of air-drying is the time required. When CO_2 is passed through sand mixed with a sodium silicate type of binder, bonding of the sand occurs due to the formation of silica gel by the action of CO_2 on sodium silicate. As silica gel loses strength during heating, it is possible that sintering may not occur. Complete data on these aspects of the process are not available.

SANDS, ADDITIVES AND THEIR PROPERTIES.

A wide variety of British and foreign sands may be used. The sands must be free from active clay, clean, dry and cold. Angular or sub-angular sand may be used, with an A.F.S. number varying from 30 to 150 and comparatively free from fines. The use of dry sands improves the strength, whereas cold sands prevent rapid hardening of the mixture on standing. The presence of clay and fines makes the moulds and cores friable, requires higher percentages of binder, decreases permeability and makes thorough gassing very difficult. Although silica gel loses its strength on heating, it has been observed with some high temperature melts that sintering may occur, resulting in collapsibility inferior to that of conventional sand practice. Certain additions, e.g., pelleted pitch, asphalt, coal dust etc., have been found to give adequate

collapsibility for foundry use. These additions, the amount of which varies from ½ to 1 per cent., are also useful in improving stripping properties. On the other hand they give rise to gas and dense fumes. Fluorspar has been reported to give promising result in that it does not give gas or fumes, yet it lessens metal penetration and increases collapsibility.

It has been reported that sands with high clay contents have been successfully used but unfortunately no data are available. It is possible however that the presence of about 1 per cent. of certain types of non-active clays may not be harmful. Active clays tend to absorb moisture. In the CO_2 process the cores and moulds are not dried by heating and therefore any moisture absorbed by the active clays will lead to scabbing and blowing of castings. Furthermore, the compression strength decreases as the clay content increases. This is especially so after long standing times, as the compression strength of clay-free sand increases with time, but that of sand containing clay decreases (eventually reaching a minimum value after 2 — 3 days). The effect of moisture on compression strength is similar to that of clay.

An approximately linear relationship exists between the optimum content of binder for maximum strength and the A.F.S. fineness number of the sand, which may be expressed as :

$$\text{"B"} = 0{\cdot}0245\ F + 1{\cdot}75 \quad (1)$$

where "B" = optimum binder content, p. cent

"F" = A.F.S. fineness number.

Once the sand is graded, the optimum binder content may be determined from the above equation. The permeability of the optimum mixture may then be estimated from the equation :

$$\text{"P"} = 196 - 6\,B \quad (2)$$

where "P" = Permeability.

This equation is applicable within the range of 1 to 7 per cent. binder to sands generally used in British foundries covering a wide range of A.F.S. numbers.

For a fixed grade of sand, and using within $\pm$ ½% of the optimum binder content, the relation between the compression strength and gassing time is given by :

$$x = 2\,t + 150 \quad (3)$$

where x = compression strength in lb./sq. in.

t = gassing time in secs. (20 - 300 secs.)

This equation is not valid for the initial 10 to 20 secs. gassing time, during which compression strength rapidly rises from 1 lb. to about 200 lb./sq. in. Although gassing times higher than 30 secs. are not usually necessary, equation (3) gives the gassing time required to attain a given compressive strength if a mould or core is required urgently and insufficient time is available for development of the necessary strength by standing after the normal 10 — 20 secs. gassing. Under normal conditions, further gassing is only a waste of gas and labour. If any core or mould is urgently needed an alternative to extra gassing is to heat for a short time. It has been reported that after the initial gassing and using 4 per cent. of a proprietary binder, the strength was about 100 lb./sq. in. This increased to 250 lb./sq. in. after ½ hour standing, but on baking the core for 20 mins., at 200° C. and then cooling, the strength had increased to 1,200 to 1,400 lb./sq. in. This may not be a typical case but undoubtedly baking at a low temperature for a short time increases the compression strength.

The moulds and cores are usually hardened either in boxes or with patterns in situ, when the green strength is only ½ to 1½ lb./sq. in. After the initial gassing, the patterns are removed with the aid of ejector pins or stripping plates. If the pattern is to be removed

before gassing, green strength in the region of 3 to 4 lb./sq. in. is required, as in conventional sand practice, where green strength is of major importance. Such a strength can be obtained with any suitable proprietary binder. Temperature affects the behaviour of sand with a sodium silicate binder in that low temperatures lead to higher compression strength and therefore poor collapsibility. Hence with low temperature castings the ratio of sand to metal thickness should be so adjusted that the outside sand reaches a temperature over 400° C. With high temperature melts, no difficulty is experienced, as the bulk of the sand, if a proper metal/sand ratio is maintained, reaches a temperature of over 600° C.

WORKING PROCEDURE AND MECHANISATION.

A conventional oil/sand mixer may be used in this process, using a milling time from 8 — 10 minutes. After milling, the sand should be kept covered by a moist rug, to avoid air hardening of the bonded sands during storing. Conventional wooden or metal patterns are in general use. Before ramming, the patterns should be painted with cellulose lacquer or silicone-oil emulsion to facilitate smooth stripping. An emulsion of linseed oil and water has also been found satisfactory. The patterns should be wiped down periodically to remove adhering sodium-silicate. Core blowing and ramming are as in conventional practice.

GASSING TECHNIQUE.

The introduction of gas into the sodium-silicate bonded sand may be carried out in several ways, depending on the individual foundry requirements and the casting design. The underlying principle is that for efficient gassing, it is desirable that a minimum amount of gas traverses the whole mass of sand within the shortest possible time. Theoretically, the amount of gas required for the reaction amounts to about 0·3—0·5 per cent. of the sand volume, but in practice, including gas lost to the atmosphere, approximately 1 per cent. is required for hardening. For efficient operation, a gas pressure of about 20—25 lb. per sq. in. has been found suitable.

The following methods have been used for introducing the gas into the sands.

(a) The gas may be introduced by inserting a hollow tube or tubes into the sand. The number of tubes and their angle of introduction will depend on the size and design of the core or mould and on the gas supply points.

(b) For small cores, gassing may be done in a closed box, provided with adjustable clips, shutters, and grids so that different types of small cores may be hardened in the same box.

(c) Hollow metal patterns may be used. The gas, which is introduced into the empty space, goes through the pattern vents, traverses the volume of sand and finally escapes through the nozzle of the cover.

In all cases it is obvious that the design should be such as to prevent escape of gas and that it should ensure that no part of the sand remains unaffected by the carbon dioxide. For very large moulds or cores, introduction of carbon-dioxide is not easy. Experiments are therefore in progress in certain British foundries on the use of fast drying materials for moulds and cores made of sodium-silicate bonded sand.

Due to the sharp fall in pressure in the valve, freezing up of carbon dioxide may occur during gassing. This trouble may be avoided by employing suitable valves or by designing the gas system so that steep pressure gradients are avoided.

ADVANTAGES OF CO_2 PROCESS.

(i) As cores and moulds do not require heating, baking stoves are unnecessary, thereby saving fuel and floor space.

(ii) The quick turnover of cores and moulds, compared with conventional practice reduces labour and floor space requirements. As the turnover is rapid the number of patterns may be reduced.

(iii) As the cores and moulds are hardened on the spot, handling is reduced considerably, thereby saving time and labour. Distortion of moulds and cores during handling is also diminished and greater dimensional accuracy is obtained.

(iv) The simple hardening technique reduces considerably the number of strengtheners required. In some cases no strengtheners are needed.

(v) The use of suitably graded dry sand and a low volatile content binder gives better permeability compared with other processes. This in turn lessens the danger of gas porosity and blowing.

(vi) The process can be introduced into any foundry working on conventional oil/sand practice without any drastic change, as it may be introduced gradually with only a small capital outlay, and existing equipment can be utilised with little modification. It is equally applicable to both batch type and jobbing foundries.

In conclusion, it should be emphasised that the success of the carbon-dioxide process depends on proper mechanisation, although even with a semi-mechanised technique, foundries using the process have found that costs do not exceed those of conventional sand practice and in some foundries it has been reported to be considerably lower. Further developments in gassing technique should ensure the future success of the process.

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FACTORS AFFECTING THE SOLUBILITY OF OXYGEN IN MOLTEN IRON IN EQUILIBRIUM WITH FeO-MnO-SiO_2 SLAGS.

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by

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I N D E X.

CHAPTER I.

INTRODUCTION.

INTRODUCTION.

Steelmaking consists essentially of the removal of impurities, such as phosphorus, silicon, carbon, etc., by a process of oxidation. The amount of oxygen which enters the molten metal will vary with the process used, the final carbon content of the metal, the iron oxide and basicity of the slag and the temperature, but in most cases is in excess of that desired in the finished steel. Deoxidation of the steel is therefore usually necessary before teeming, the extent of deoxidation required depending on the type of ingot to be produced, i.e., whether rimmed, semi-killed or fully killed steel is desired.

Oxygen may be removed by a (i) diffusion process into a low iron oxide type of slag, as in electric steelmaking, (ii) by carbon, in which case the product is "CO" which escapes to the atmosphere. As carbon is introduced into the metal, the extent of carbon deoxidation which may be carried out may be limited by the carbon specification of the final steel, (iii) by the addition of metals which have a higher affinity for oxygen than iron and whose oxides are relatively insoluble in the molten iron. The oxides, produced by the reaction, precipitate out either as liquid or solid deoxidation products. "Precipitation deoxidation" is the most widely practised method, as the removal of oxygen is rapid, the degree of deoxidation is fairly easy to control and the demanded specification may be met within permissible accuracy. The elements used in precipitation deoxidation must not only have a

greater affinity for oxygen than iron, but must also dissolve quickly in the metal bath and give rise to deoxidation products which separate and rise rapidly from the molten metal bath. As they must also remain dissolved to some extent in the liquid steel, the residual amount must meet the specification of the steel being produced.

Elements which may be used as deoxidizers in precipitation deoxidation are Mn, Si, Al, Zr, Be, etc., although the first three are the most commonly used. All dissolve rapidly in the molten metal but the rate of separation of the deoxidation products depends mainly on their shape and size, as in all cases they are considerably less dense than steel. The rate of rise of the products increases as the particle diameter increases and the more nearly the shape approaches that of a sphere. When the deoxidation products are liquid, they not only more nearly approach the spherical shape but they can also increase in size by coalescence with other particles. Solid deoxidation products are usually irregular in shape and also would not be expected to coalesce with other particles. Thus for efficient separation of the deoxidation products, it is preferable that they should be liquid. Liquid deoxidation products are more likely to arise from the use of double-deoxidisers, e.g., Mn-Si alloys, rather than single elements, as the appropriate phase diagrams indicate that the resultant mixed oxides usually have lower melting points than the single oxides. Manganese silicates can melt at temperatures as low as 1200°C as compared with melting points of 1785°C and 1713°C for MnO and SiO_2 respectively.

As the reactions which take place between most deoxidisers and

molten iron are believed to be rapid, their rate being largely controlled by diffusion process(1), the oxygen content of the metal after addition of deoxidiser will be determined by the equilibrium between molten metal and the deoxidation product. In the most commonly practised method of deoxidation in which ferro-manganese, ferro-silicon, and silicon-manganese alloys are used, the deoxidation product consists of either liquid iron-manganese silicates or globules of glassy silica depending on the manganese/silicon ratio in the deoxidisers used. In order to obtain further information on the deoxidation of iron with manganese and silicon, an investigation has been made of the equilibrium between molten iron and iron-manganese silicate melts, with particular reference to the oxygen content of the metal at equilibrium. Because in steel works practice, the formation of deoxidation products and the reduction of the oxygen content of the metal will continue as the temperature of the metal falls to its freezing point, the effect of temperature on the equilibrium oxygen content has also been studied within the range of temperature possible with the furnaces available. It is then possible to calculate the most appropriate deoxidiser for a given steel and the extent of deoxidation which may be expected from its use. A measure of the effectiveness of deoxidation can be obtained from the results of experiments in which a weighed amount of manganese-silicon deoxidiser of known composition is added to molten iron containing a known percentage of oxygen.

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CHAPTER 2.

DISCUSSION OF PREVIOUS WORK.

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(a) The Solubility of Oxygen in Liquid Iron.

Molten iron dissolves oxygen and the solubility of oxygen in molten iron increases with increasing temperature. The solubility of oxygen is low due to the formation of a liquid iron oxide phase of variable composition. Figure 1 shows the Fe-O phase diagram(2,2a), from which the compositions of the metal and the iron oxide phase in equilibrium at any temperature can be read. The latter phase, although usually called ferrous oxide, contains more oxygen than the stoichiometric formula FeO. The composition has been reported to be $Fe_{0.95}O$ at 1600°C. by Richardson and Jeffes and Withers(3), and its free energy of formation is given by

$$0.95Fe(L) + \tfrac{1}{2}O_2(g) = Fe_{0.95}O\ (L)$$

$$\Delta G^{\circ} = -59{,}050 + 12.05T.$$

In discussions on steelmaking reactions this phase is normally referred to as ferrous oxide and will be referred to as such here.

The oxygen pressure at which this phase appears is approximately 0.8×10^{-3} atmosphere at 1600°C and cannot be measured directly. Hence indirect methods, such as the equilibria between the oxide and a CO/CO_2 or H_2/H_2O gas mixture have been used.

The direct determination of the solubility of oxygen in liquid iron, presents many practical difficulties. The iron-oxygen solution attacks all the known refractories in which melts may be carried out and contamination of both the iron oxide and the metal phase may occur. Under such conditions, the oxygen solubility obtained is no longer that corresponding to pure ferrous oxide but is that in equilibrium with an

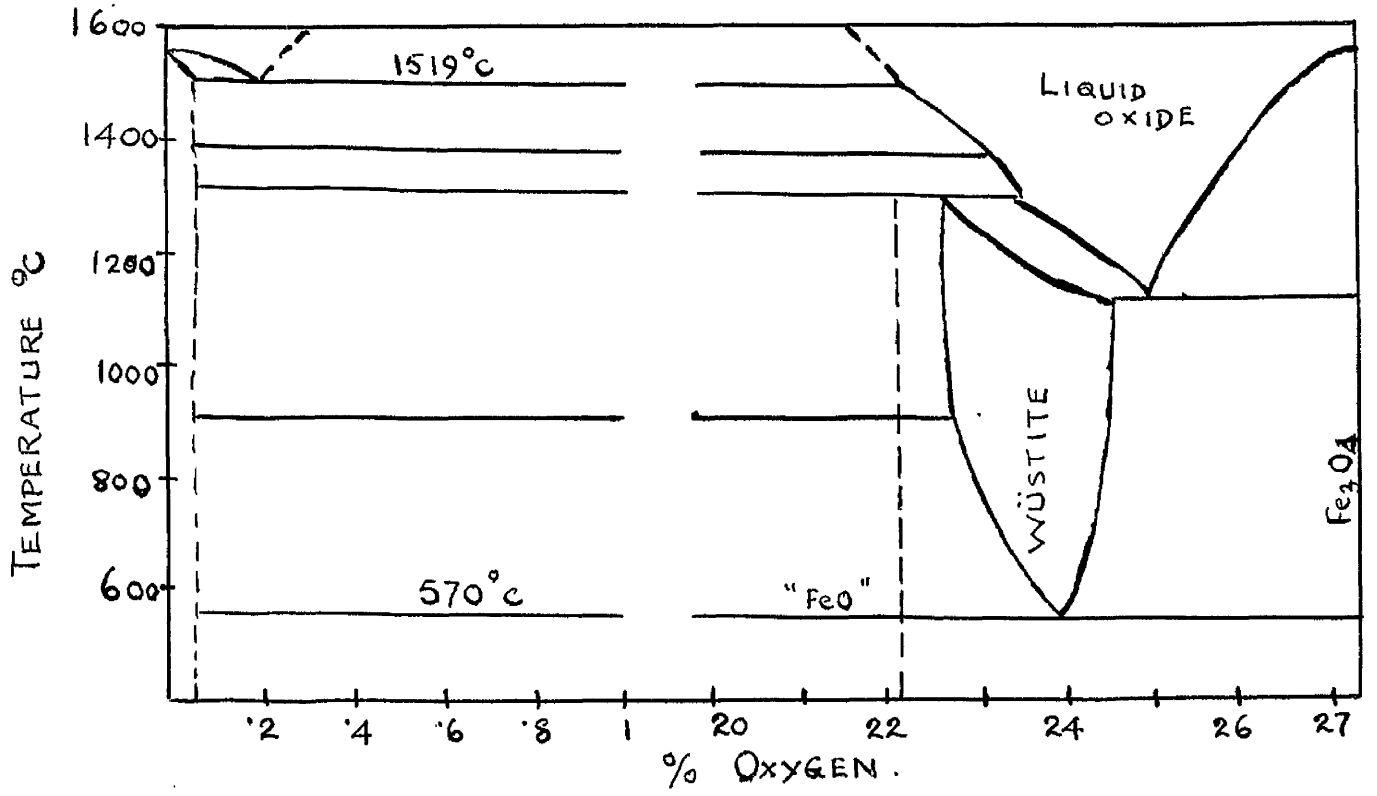


FIG. 1a. IRON-OXYGEN PHASE DIAGRAM (WHITE[2])

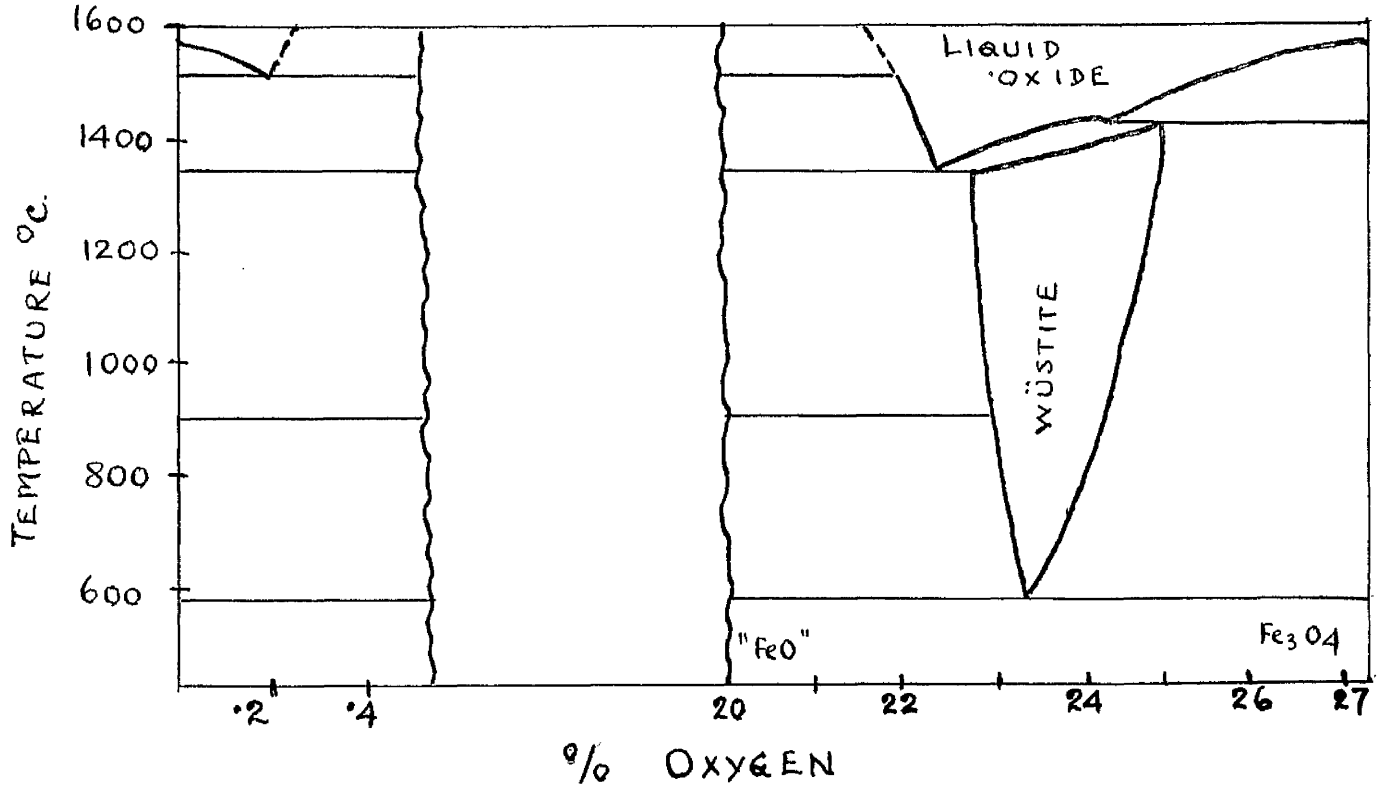


FIG. 1b. IRON-OXYGEN PHASE DIAGRAM (DARKEN AND GURRY[2a])

(FeO,MO) Slag system, where MO indicates the refractory oxide taking part in the reaction. If the amount of impurity introduced is small and forms an ideal solution with FeO, it is possible to calculate the saturation limit of oxygen in pure iron at any desired temperature by proportion.

Amongst the earlier workers, Ledebur(4), Rommeff(5) and Fritton and Hansen(6) reported the solubility of oxygen at the freezing point of iron to be 0.24%, 0.29% and 0.21% respectively. On the basis of Ledebur's result(4), Le Chatelier(7) accepted a solubility value of 1.1% FeO, corresponding to 0.244% of oxygen at 1600°C.

Later, Herty and Gaines(8) reported the oxygen solubility to be,

$$O\% = 0.1475 \times 10^{-3} \cdot t - 2.080$$ where 't' is in °C.

This gives oxygen solubilities at 1550°C and 1600°C of 0.25% and 0.32% respectively. Korber and Oelsen(9) reported almost the same values as Herty and Gaines(8). Their equation being

$$O\% = 0.13 \times 10^{-3} \cdot t - 1.77$$ where "t" is in °C.

Chipman and Samarin(10) and Kuntz and Chipman(11) studied the equilibrium between molten iron and H_2/H_2O gas mixture and found the solubility of oxygen in liquid iron at 1600°C to be 0.22 percent which is considerably lower than the values obtained by earlier workers. Their results also indicated that the solution of oxygen in liquid iron obeyed Henry's Law up to saturation value, so that in the absence of other alloying elements the activity of oxygen is directly proportional to its concentration.

Chipman and Fetters(12) determined the solubility of oxygen by melting iron in magnesia crucible in a high frequency furnace; slags consisted of iron oxide containing small percentages of magnesia and lime picked up from the crucible. Their solubility data are given by the relationship

$$\text{Log } \underline{O}\% = \frac{-4869}{T} + 1.935 \quad \text{where "T" is in °K.}$$

This indicates an oxygen solubility of 0.155% and 0.23% at 1550°C and 1600°C respectively. It should be noted that Chipman and Fetters(12) did not make any correction for the presence of impurities in the slag, as they found that the solubility was independent of the composition of the slag when the slag contained more than about 90 percent iron oxide. In order to avoid contamination by crucible material, Taylor and Chipman(13) melted slag and metal in a magnesia crucible in a rotating crucible furnace. The oxygen solubility values obtained were slightly higher at higher temperatures than those of Chipman and Fetters(12), nevertheless both sets of data could be represented satisfactorily by the relationship

$$\text{Log } \underline{O}\% = \frac{-6320}{T} + 2.734, \quad \text{where "T" is in °K.}$$

This corresponds to oxygen solubilities of 0.186% and 0.28% at 1550°C and 1600°C respectively.

Fischer and Von Ende(14) who also used a high frequency furnace with magnesite crucibles obtained oxygen solubilities of the same order as those obtained by Chipman et al (10,11,12,13). Bell, Murad and Carter(15), reported an oxygen solubility in liquid iron at 1550°C

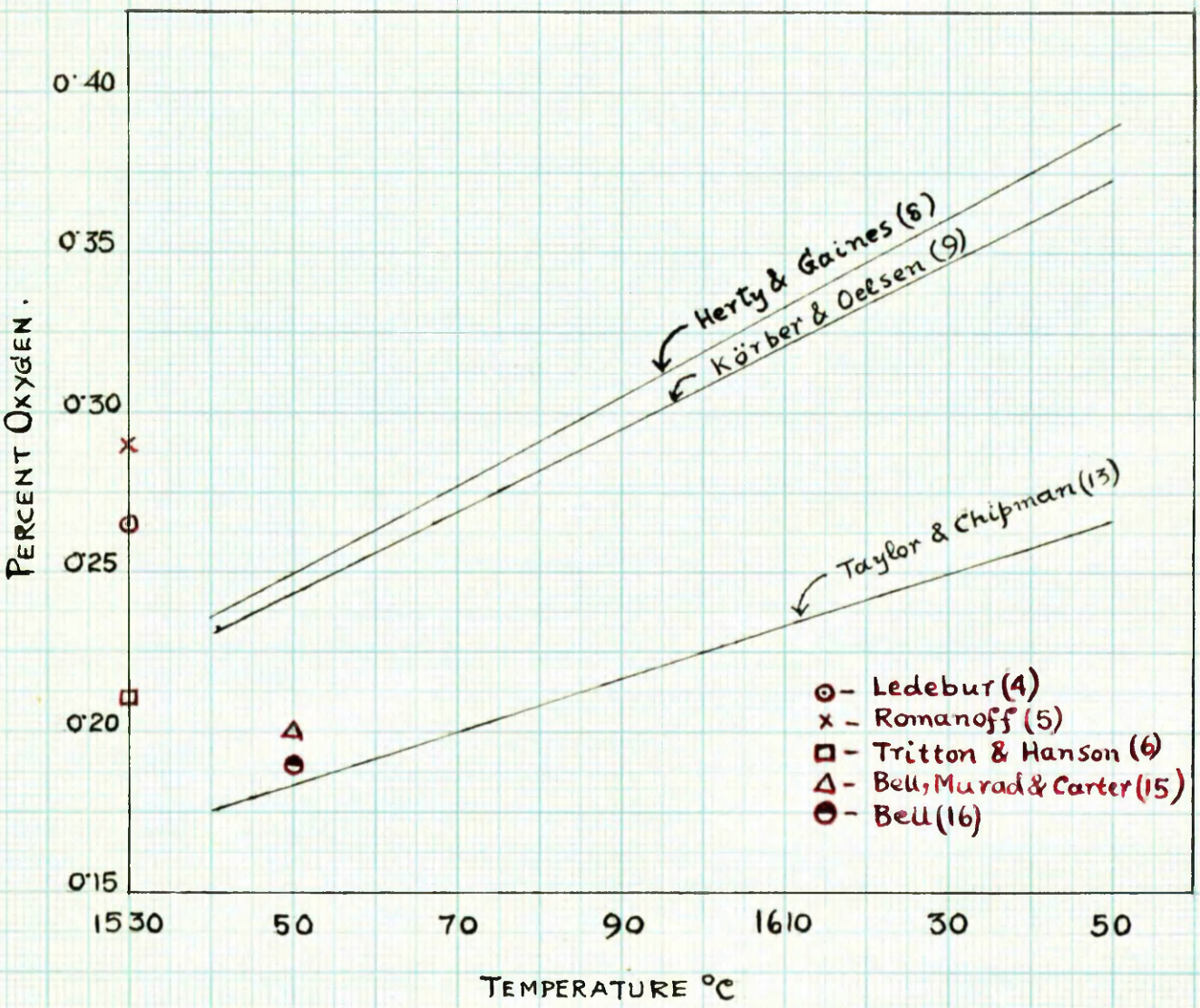


FIG. 2. EFFECT OF TEMPERATURE ON THE SOLUBILITY OF OXYGEN IN LIQUID IRON.

of 0.20% from the results of slag-metal equilibrium experiments carried out in magnesia crucibles rotated in a high frequency furnace. In similar experiments, but using a resistance furnace, Bell(16) obtained a value of 0.19% at 1550°C.

It will be seen from Figure 2 that the oxygen solubility values obtained by early workers(4-9) are much higher than those obtained in more recent experimental work. The most probable source of the discrepancy is in temperature measurements, as Chipman and Fetters(12) and Taylor and Chipman(13) have shown that the nature of the atmosphere and the sampling technique have little influence on oxygen solubility.

(b) Manganese-Oxygen Equilibrium in Liquid Iron.

When manganese is added as a deoxidiser to a bath of molten iron containing oxygen, dissolved oxygen is removed from the solution in the form of deoxidation products, the reaction occurring being

$$\underline{FeO} + \underline{Mn} \rightleftharpoons (MnO) + \underline{Fe}$$

At equilibrium $$K_{Mn} = \frac{(a_{MnO})}{(a_{FeO})\,[a_{Mn}]}$$

the activity of iron being taken as unity. At normal deoxidation temperatures (Mn,Fe)O deoxidation product may be liquid or solid depending on its composition, since ferrous oxide melts at 1370°C and manganous oxide at 1785°C. The most recent investigation of the FeO-MnO phase diagram is that of Schenck, Schmahl and Biswas(17) whose results are depicted in Figure 3, from which it can be seen that FeO and MnO form a continuous series of solid solution. The work of Foster and Welch(18) has shown that (FeO.MnO) solid solutions are thermodynamically ideal over the whole range of composition. Because of similarity in molecular weight and ideality in binary solution of FeO and MnO, it is permissible to use weight percentages instead of activities and the equilibrium constant obtained in this way can be regarded as the true equilibrium constant. Thus K_{Mn} can be written as,

$$K_{Mn} = \frac{(\%MnO)}{(\Sigma\%FeO)[\%Mn]}$$

provided that concentration of manganese in molten iron is small and that iron-manganese solutions behave ideally.

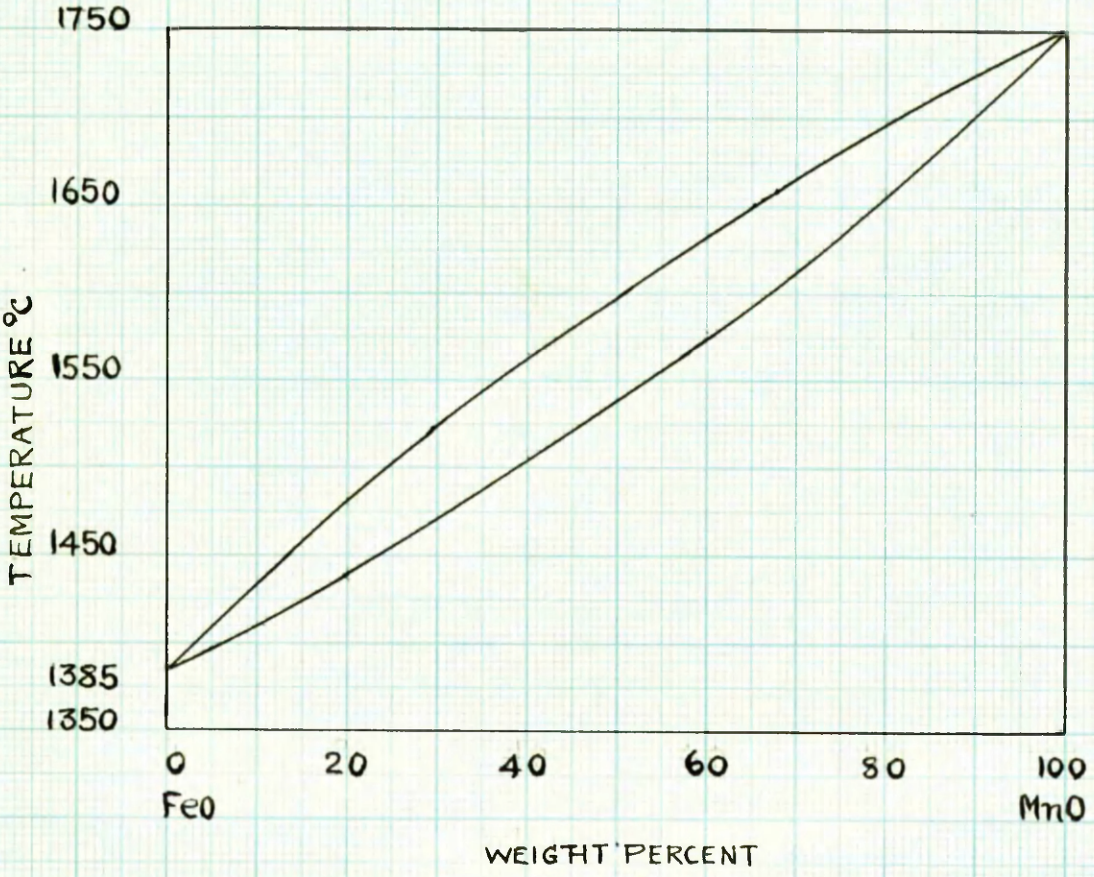


FIG. 3. FeO - MnO PHASE DIAGRAM (17).

K_{Mn} has been determined by several investigators from the results of slag-metal equilibria experiments, but in all cases interpretation of the results is complicated somewhat due to contamination of the FeO-MnO slags by the crucible material.

Krings and Schackmann(19) carried out their experiments at 1550°C to 1560°C in magnesia and alumina crucibles and obtained $K_{Mn} = 3 \cdot 1 \pm 0 \cdot 5$. Although their slag contained up to 30% Al_2O_3 and 21% MgO, it was not possible to observe any effect that the crucible material might have on K_{Mn}. It should be pointed out, however, that unless magnesia has a marked lowering effect on the melting point, which seems unlikely, the FeO-MnO diagram of Schenck et al(17) indicates that many of the slags used would be solid or partially solid at the experimental temperature. It is probable that the same is true for the slags of high Al_2O_3 content. It seems more probable that the experimental temperatures were considerably higher than 1550°C-1560°C, caused by low optical pyrometer reading. At the same time, Korber and Oelsen(9) carried out experiments in magnesia crucibles over a wide range of temperature (1490°C-1880°C) and reported the relation between temperature and K_{Mn} in the form of the equation

$$\log K_{Mn} = \frac{6234}{T} - 1.0268, \quad \text{where "T" is in °K.}$$

From this the values of K_{Mn} at 1550°C, 1600°C and 1700°C are 2.5, 2.0 and 1.4 respectively.

Gero, Chipman and Winkler(20) supplemented earlier data obtained by Winkler and Chipman(21) with the results of experiments carried out in large magnesia crucibles heated by induction with electrodes over the melt to keep the slag layer molten; temperatures were measured by Mo-W thermocouple encased in silica tube. Their slags consisted of FeO, MnO, MgO with small percentages of lime and silica picked up accidentally from the crucible and thermocouple sheath. The plot of log K_{Mn} against $\frac{1}{T}$ obtained from the combined data showed considerable scatter and the slope of the line which was finally drawn through the points was obtained from a theoretical consideration of the manganese reaction. Two values of the constant were used, K_{Mn}, based on the use of ΣFeO, and K_{Mn}^{*}, based on the use of analytically determined FeO. Their relations with temperature were expressed as,

$$\text{Log } K_{Mn} = \frac{6440}{T} - 2.95$$

giving K_{Mn} values at 1550°C, 1600°C and 1700°C of 3.8, 3.1 and 2.1 respectively.

$$\text{Log } K_{Mn}^{*} = \frac{6760}{T} - 3.09$$

giving K_{Mn}^{*} values at 1550°C, 1600°C and 1700°C of 5.2, 4.3 and 2.8 respectively.

Turkdogan and Pearson(22) calculated statistically the best line to draw through the points of Chipman, Gero and Winkler(20) and

obtained the K_{Mn} - temperature relationship

$$\text{Log } K_{Mn} = \frac{7406}{T} - 3.436$$

which gives K_{Mn} values of 4.2, 3.3 and 2.1 at 1550°C, 1600°C and 1700°C respectively.

Bell(16) carried out a small number of experiments in magnesia crucibles in the absence of silica at 1550°C and reported an average value of 3.6 for K_{Mn}.

It will be seen that the more recent determinations of K_{Mn} are considerably higher than those of Krings and Schackmann(19) and Korber and Oelsen(9) probably because of errors introduced in the use of optical pyrometers for temperature measurements by the latter workers.

The value of K_{Mn} has been calculated from theoretically available thermodynamic data by Chipman, Gero and Winkler(20) and Schenck, Schmahl and Biswas(17). The former obtained $\log K_{Mn} = \frac{6440}{T} - 2.62$, giving K_{Mn} values at 1550°C, 1600°C and 1700°C of 5.1, 4.1 and 2.8 respectively. These values are in excellent agreement with those derived from the equation for $\log K_{Mn}$ which is based on the use of FeO, not $\leq$ FeO. Schenck et al(17) obtained the equation,

$$\text{Log } K_{Mn} = \frac{6936}{T} - 3.03$$

from which K_{Mn} values of 6.3, 5.0 and 3.2 at 1550°C, 1600°C and 1700°C respectively can be calculated.

K_{Mn} values obtained by the various workers are compared in Table 1.

TABLE 1.
Values of K_{Mn}.

Temp. °C.	Krings and Schackmann (19)	Körber and Oelsen(9)	Chipman, Gero and Winkler (20)	Turkdogan and Pearson (22)	Bell (16)	Schenck Schmahl and Biswas(17)
1550	3.1±0.5	2.5	3.8	4.2	3.6	6.3
1600	-	2.0	3.1	3.3	-	5.0
1700	-	1.4	2.1	2.1	-	3.2

Hilty and Crafts(23) failed to determine K_{Mn} in rotating crucible experiments, due to the fact that the FeO-MnO slags crept up the sides of the rotating metal cup. However, they reported a relationship between manganese and oxygen concentrations in molten iron in equilibrium with (FeO, MnO) deoxidation products which agreed well with that given by Chipman, Gero and Winkler(20). Likewise, Sloman and Evans(24) in a study of deoxidation of iron by manganese at the melting point of iron were unable to obtain values of K_{Mn} as the deoxidation product could not be analysed directly. The results agreed well with the theoretical equilibrium between iron and solid FeO-MnO slags at the melting point of iron as calculated by Kubaschewski(25). Isolation of the inclusions by the alcoholic-iodine method indicated that the two oxides were completely miscible and that above 0.7% manganese in the metal, the deoxidation product contains more than 90% MnO.

It is probable that the effect of manganese on the activity coefficient of oxygen is small. Richardson(26) suggests that as the affinity of manganese for oxygen is intermediate between that of chromium and vanadium for oxygen, 0.5% and 1.0% manganese may lower f_O to 0.9 and 0.8 respectively. On the other hand Chipman(27) has referred to experiments which indicate that f_O is not appreciably affected by the presence of several percent of manganese in metal. This is in agreement with the observation(9) that the ratio of FeO/MnO slags to $\underline{O}$ in liquid metal is not affected by the presence of manganese. It seems reasonable to assume that the effect of manganese in the concentrations encountered in the present work on the activity of oxygen may be ignored.

(c) Silicon-Oxygen Equilibrium in Liquid Iron.

In the production of semi-killed and killed steel, silicon is added as a deoxidiser. The reaction occurring and the corresponding equilibrium constant may be represented as,

$$\underline{Si} + 2\underline{O} \rightleftharpoons (SiO_2)$$

$$K_{Si} = \frac{a_{SiO_2}}{[a_{Si}]\,[a_O]^2}$$

When an excess of silicon is added, the deoxidation product is silica but if the silicon added is insufficient, it might be possible to form a silica saturated iron silicate slag as well as solid silica. This would not normally occur in practice as the corresponding activity of FeO in the deoxidation product would correspond to far too high an oxygen content. (In the presence of manganese, the interpretation is more complex and will be referred to in more detail later). Theoretically with decreasing amounts of silicon added, it should be possible to produce unsaturated iron silicate inclusions, which would subsequently solidify inaccordance with the FeO-SiO_2 phase diagram. The usually accepted form of this is that given by Bowen and Schairer(28) and depicted in Figure 4. Schenck and Wiesner(29) have recently investigated the equilibrium between liquid iron and silica saturated iron silicate slags and from the results obtained suggest a slight modification to the silica liquidus curve. Their proposed curve is also shown in Figure 4.

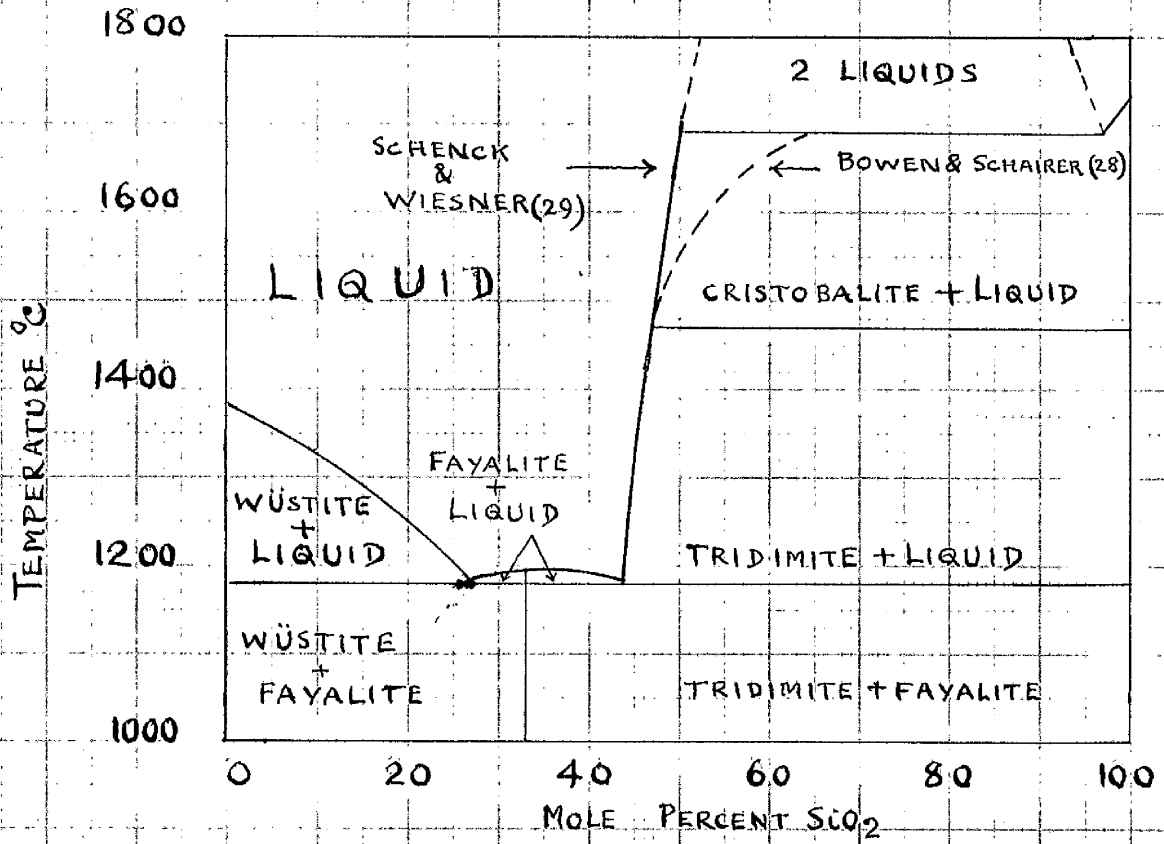


FIG. 4. $FeO - SiO_2$ PHASE DIAGRAM

(BOWEN & SCHAIRER[28]; MODIFICATION TO SiO_2 LIQUIDUS CURVE – SCHENCK & WIESNER (29))

The variation of activities in the binary $FeO-SiO_2$ system, has been investigated by Taylor and Chipman(13) and Schuhmann and Ensio(30). Taylor and Chipman, in rotating crucible experiments determined the solubility of oxygen in liquid iron in equilibrium with iron silicate slags and found that FeO behaved ideally in $FeO-SiO_2$ slags up to the limit of silica saturation. In the $FeO-SiO_2$ system, a compound, fayalite, occurs at the composition $2FeO.SiO_2$ and there exists a range of immisci-bility at the high silica end of the diagram as shown in Figure 4. Compound formation is usually associated with negative deviations from Raoult's Law whereas liquid immiscibility is usually accompanied by positive deviation. It mightthereforo have been expected that some evidence of these deviations would have been shown by the results of Taylor and Chipman; it is probable that the experimental method used was not accurate enough to show such deviations, which were later detected by Schuhmann and Ensio(30), who studied the equilibrium of CO/CO_2 gas mixture-$FeO-SiO_2$ slags in iron crucibles. They found that FeO showed a slight positive deviation up to about 27 mole percent of silica after which the deviation was negative up to silica saturation. Activities of SiO_2, calculated by the Gibbs-Duhem equation are shown in Figure 5. Schuhmann and Ensio(30) expressed the variation of a_{FeO} at silica saturation with temperature as,

$$\text{Log } a_{FeO} = \frac{2090}{T} - 0.590$$

over a temperature range from 1250°C to 1400°C. It is evident that the

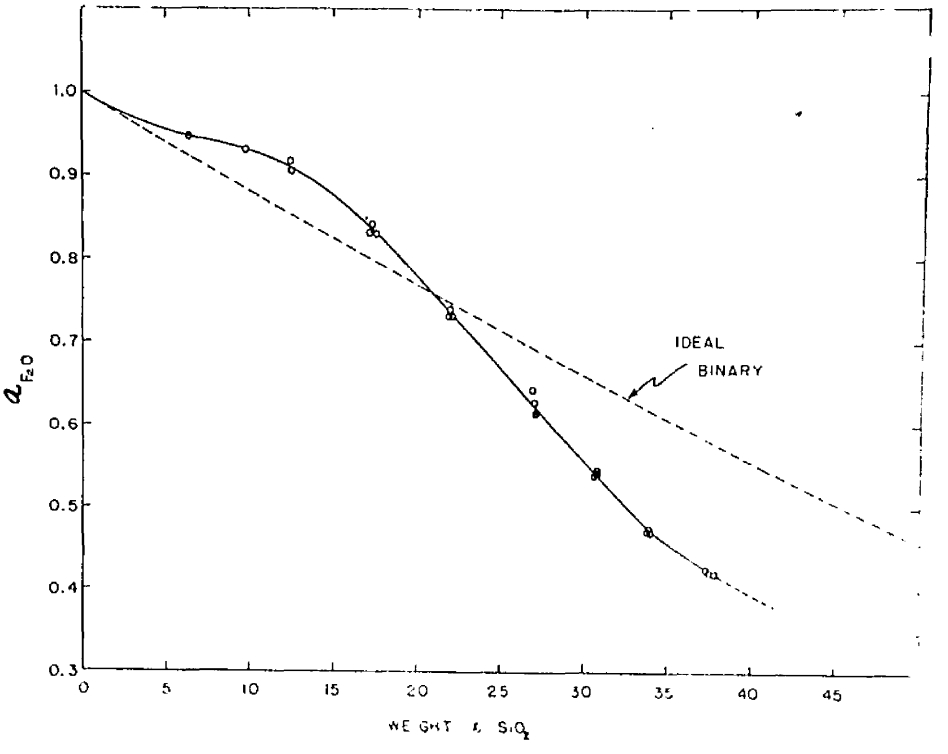


FIG. 5. VARIATION OF a_{FeO} WITH SILICA CONTENT IN $FeO-SiO_2$ SLAGS AT 1250°C – 1400°C. (SCHUHMANN & ENSIO)[30].

variation of ^{a}FeO in silica saturated slags with temperature is fairly small. Schenck and Wiesner(29) obtained a similarly small variation which they expressed as,

$$\text{Log } {}^{a}FeO = \frac{200}{T} - 0.522$$

over the temperature range 1540°C-1730°C. Gokcen and Chipman(31) in an experimental study of the equilibrium of molten iron with H_2O/H_2 gas mixture using silica crucibles found that the oxygen saturation value of molten iron under silica saturated $FeO-SiO_2$ slags at 1600°C to be 0.088%. This corresponds to an activity of FeO of 0.39 compared with a value of 0.377 at the melting point of iron which can be obtained by extrapolating the lower temperature data of Schuhmann and Ensio(30) and 0.38 which can be calculated from the equation given by Schenck and Wiesner(29).

When the silicon reaction occurs in the presence of solid silica, as would be the case in the acid open-hearth furnace or in experiments carried out in silica crucibles, the expression for the silicon equilibrium constant can be reduced to the form

$$K'_{Si} = [{}^{a}Si].[{}^{a}O]^{2}$$

Since $^{a}SiO_2 = 1$.

Introducing weight percentages instead of activities the equation becomes

$$K_{Si} = [\%Si].[\%O]^{2}$$

Two approaches have been made to the study of this equilibrium, viz., gas-metal reactions and slag-metal reactions. Gas-metal equilibria have been studied by Zapffe and Sims(32) and Gokcen and Chipman(31). Zapffe

and Sims(32) carried out experiments in which molten iron contained in silica crucibles was brought into equilibrium with H_2O/H_2 gas mixtures. Although the oxygen content of the molten metal was determined in only a few cases, they were able to report that the product $[\%Si].[\%O]^2$ may not actually be a constant and that silicon may affect the activity coefficient of oxygen in iron. To explain this they assumed that part of the silicon exists as SiO at higher silicon levels. Gokcen and Chipman(31) investigated the same system but modified the technique to avoid errors due to thermal diffusion and to the possibility of not allowing sufficient time to reach equilibrium. In their studies of the reactions,

$$SiO_2(s) \rightleftharpoons \underline{Si} + 2\underline{O}, \quad K_1 = [\%Si].[\%O]^2$$

$$SiO_2(s) + 2H_2 \rightleftharpoons \underline{Si} + 2H_2O, \quad K_2 = [\%Si]\left(\frac{H_2O}{H_2}\right)^2$$

they plotted the oxygen content of the metal against the H_2O/H_2 ratio. After the saturation oxygen value in the melt was reached, increasing H_2O/H_2 ratio did not alter the oxygen content any further. Gokcen and Chipman(31) found that the oxygen saturation value of molten iron under a silica saturated $FeO-SiO_2$ slag to be 0.030% at 1600°C and the corresponding silicon content, according to their best estimate, was 0.003%±0.001%. The value of $[\%Si].[\%O]^2$ was almost constant over a long range of concentration, the mean value at 1600°C being 2.8×10^{-6}. The greatest deviations were observed at very low silicon contents where the silicon analysis is inaccurate and at very high silicon concentrations, where the correspondingly low oxygen contents are also less accurate. A plot of their data is shown in Figure 6. A combination of their results with

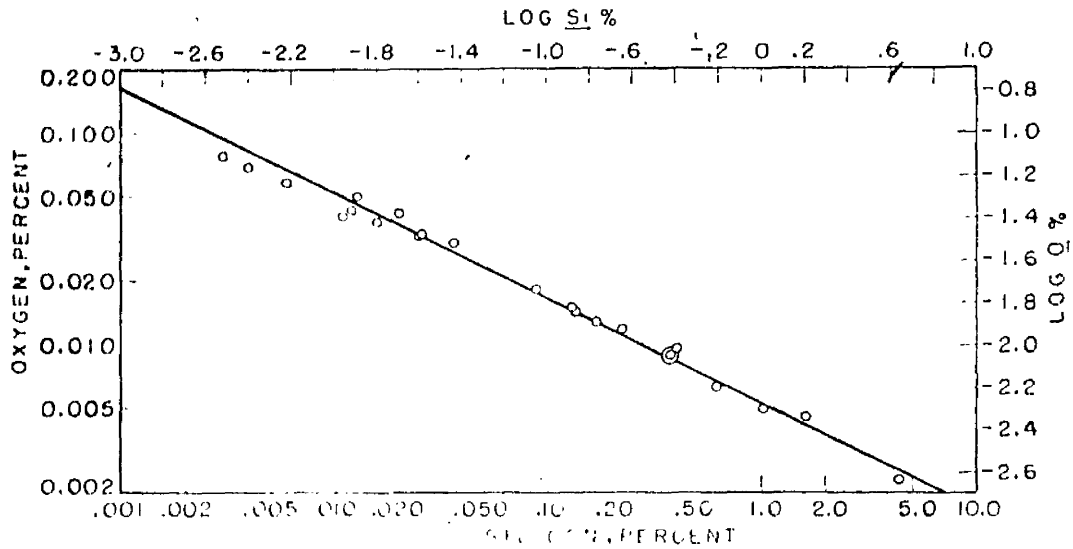


FIG. 6. Si-O EQUILIBRIUM AT 1600°C (GOKCEN & CHIPMAN)[31].

the gas-metal equilibrium data of Dastur and Chipman(33) indicated that silicon reduced the activity coefficient of oxygen as shown in Figure 7. A comparison of Figures 6 and 7 indicates a discrepancy in that the lowering of f_O by silicon, shown in Figure 7, is not in agreement with the slight raising of the activity coefficient of silicon by oxygen which can be deduced from the position of the three lowest silicon points with respect to the line of Figure 6. In a later paper Golcon and Chipman(34) withdrew Figure 7, because of the fact that subsequent work of a similar nature with Fe-Al-O system could not be reconciled with the data of Dastur and Chipman(33). Qualitatively, however, Chipman still believed that f_O was reduced by silicon and suggested that the constancy of the product $[\%Si].[\%O]^2$ indicated a compensating effect of f_{Si} and f_O within the range of 0.02% to 15% silicon. For the equilibrium,

$$SiO_2(\text{orig}) \rightleftharpoons \underline{Si} + \underline{2O}$$

they gave the value

$$\Delta G^\circ = +133,314 - 50.97T$$

$$\log K = \frac{-29150}{T} + 11.01$$

where $K = [\%Si].[\%O]^2$.

Several investigators have used slag-metal data to calculate the equilibrium constant of the silicon reaction. The earliest investigations were based largely on a study of Acid Open-hearth data from which Herty and co-workers(35) obtained 0.82×10^{-3} at 1600°C for the product $[\%Si].[\%O]^2$ and Schenck and Bruggemann(36) obtained 1.76×10^{-3}. An

important laboratory investigation was that of Korber and Oelsen(37) who melted iron under FeO-MnO-SiO_2 slags in silica crucibles and obtained 1.36×10^{-3} and 3.6×10^{-3} at 1550°C and 1600°C respectively for the above product. Although there was considerable scatter in the results obtained Korber and Oelsen(37) observed no obvious trend in the value of the constant with the composition of the metal or the slag. An optical pyrometer which was checked against a platinum-platinum/Rhodium thermo-couple was used for temperature measurement.

Hilty and Crafts(23) conducted their experiments in a rotating crucible furnace, using SiO_2, Al_2O_3 and MgO crucibles. Owing to the creeping tendency of their slags in the rotating cup, they were unable to obtain slag samples. From their metal analysis data, they plotted a series of graphs relating the silicon and oxygen contents of the metal for temperatures ranging from 1550°C to 1650°C. Typical plots are shown in Figure 8 from which it can be seen that different crucibles had no appreciable effect on the Si-O equilibrium. It will be seen that the relationship between silicon and oxygen is represented by two intersecting curves. The intersection point was explained as the point of equilibrium between the three phases, solid silica, liquid silicate and liquid iron. However, Darken(38) has pointed out that the metastable extension of the two solubility curves extend into the homogeneous field (molten iron) rather than outside which is contrary to the fundamental principles of heterogeneous equilibria. A further discrepancy in Hilty and Craft's(23) results appears to be that they indicate too low oxygen content in molten

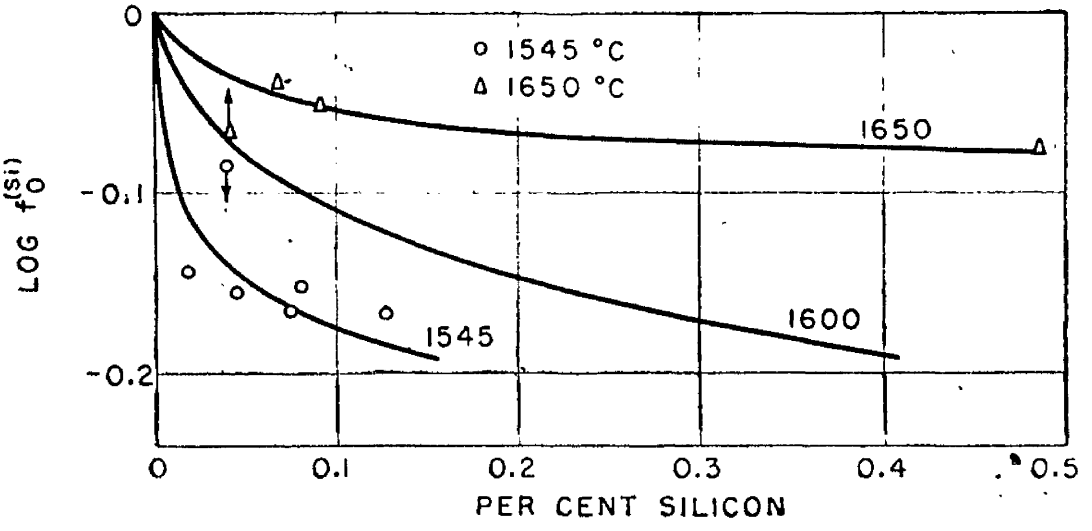
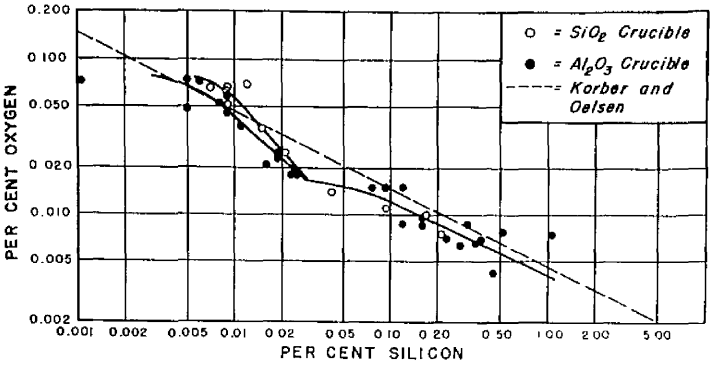
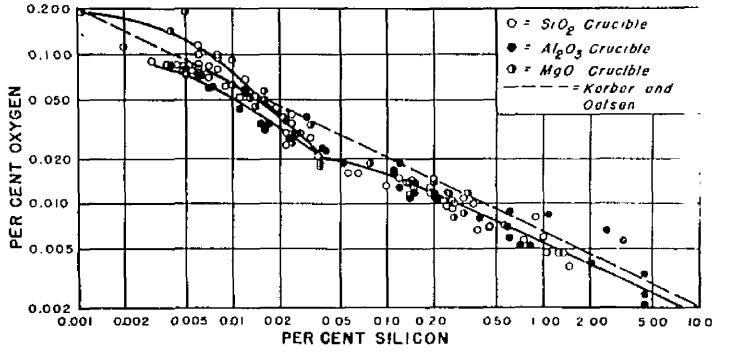


FIG. 7. EFFECT OF SILICON ON THE ACTIVITY COEFFICIENT OF OXYGEN (GOKCEN & CHIPMAN)[31].

1550°C



1600°C



1650°C

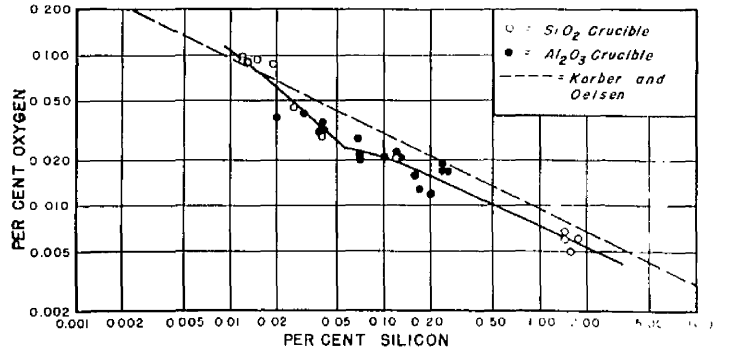


FIG. 8. Si-O EQUILIBRIUM IN LIQUID IRON (HILTY & CRAFTS)[23].

iron in equilibrium with silica saturated FeO-SiO_2 slags. Thus Figure 8 shows a value of 0.02% oxygen at 1600°C as compared with 0.030% obtained by Gokcen and Chipman(31). Nevertheless, the data of Hilty and Crafts(23) gave useful information on the silicon-oxygen equilibrium and are compared with the results of Korber and Oelsen(37) and Gokcen and Chipman in Figure 9.

Evans and Sloman(30) have also studied the deoxidation of iron by silicon in Al_2O_3 crucibles at 1527°C, the freezing point of iron. Little useful information was obtained on the silicon-oxygen equilibrium and their observation that below 0.03% silicon, pure silica was no longer deoxidation product, the corresponding oxygen content being 0.02%, is at variance with the results of Gokcen and Chipman(31) and Fischer and Von Ende(14), but agrees to some extent with the results of Hilty and Crafts(23).

Schenck and Wiesner(29) have recently determined K_{Si} from slag-metal equilibrium experiments using SiO_2 saturated iron-silicate and iron-manganese silicate slags. They obtained,

$$\log K_{Si} = \log[\%Si].[\%O]^2 = -\frac{20050}{T} + 5.750$$

from which can be calculated $K_{Si} = 1.74 \times 10^{-3}$ and 3.8×10^{-3} at 1540°C and 1600°C respectively. These figures apply to silica saturated iron silicate slags. Schenck and Wiesner also found that the addition of 30-40 percent MnO reduced K_{Si} at 1540°C to about 0.6×10^{-3} as shown in Figure 10. This variation of K_{Si} with slag composition was not observed by Bell(16) who found in slag-metal experiments using silica saturated FeO-MnO-SiO_2 slags at 1550°C, that the relative proportions of FeO and

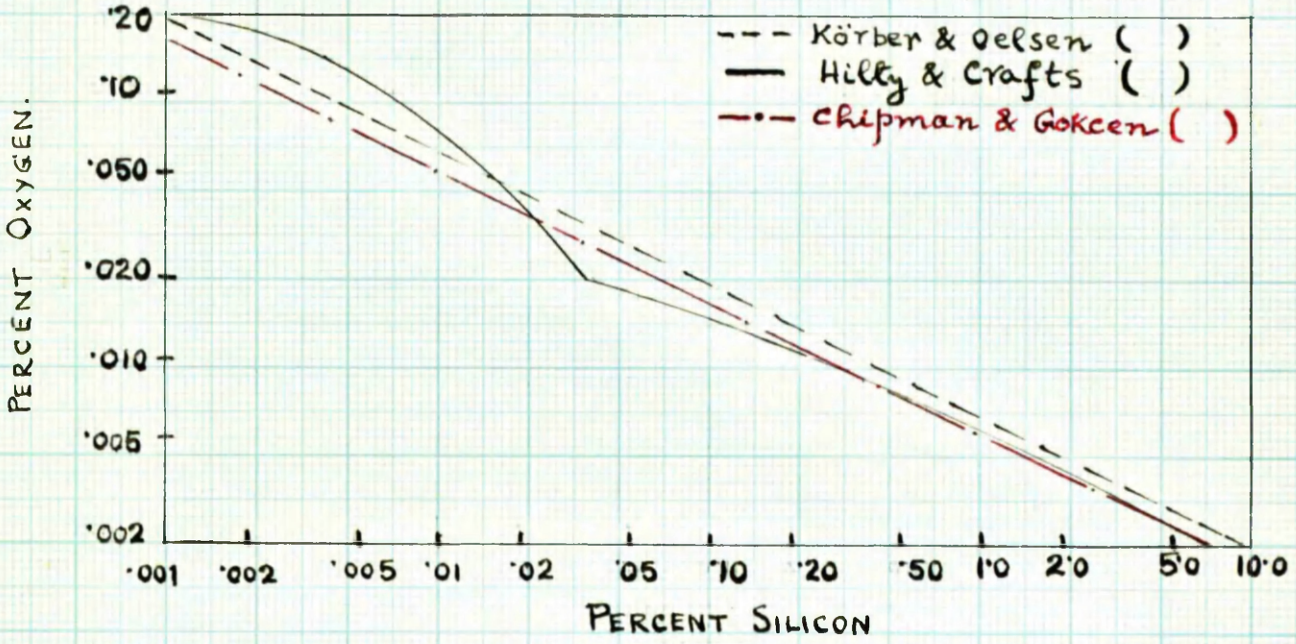
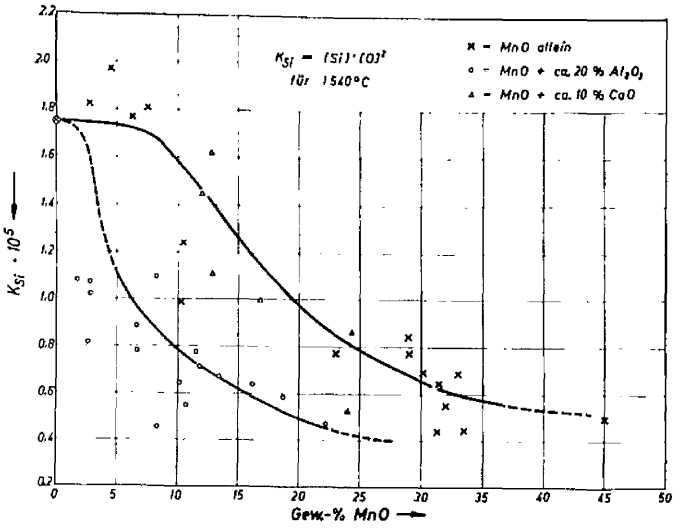


FIG. 9. SILICON - OXYGEN RELATIONSHIP IN MOLTEN IRON AT 1600°C.

(a)



(b)

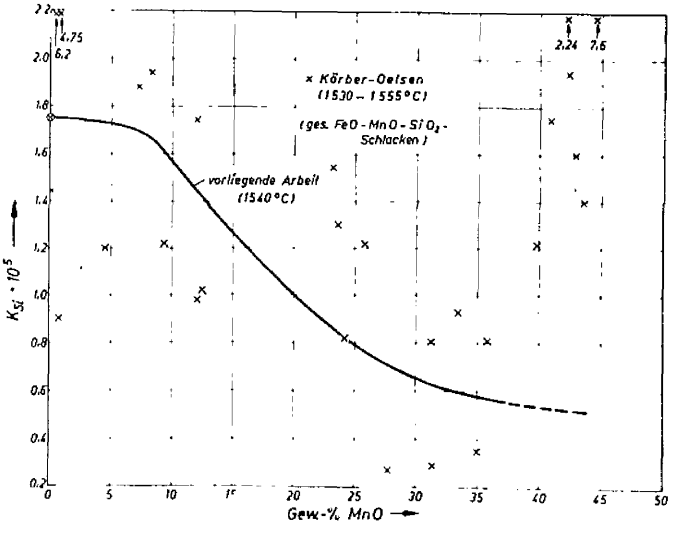


FIG. 10. EFFECT OF MnO CONTENT OF SLAG ON K_{Si}.

(a):- WORK OF SCHENCK & WIESNER (29).

(b):- MEAN LINE DRAWN BY SCHENCK & WIESNER ON KÖRBER & OELSENS EXPERIMENTAL POINTS.

MnO did not affect the silicon-oxygen equilibrium as was also found by Korber and Oelsen(37). The value of K_{Si} at 1550°C obtained by Bell(16) is 1.3 x 10^{-3}.

The values of K_{Si} obtained by the above workers are compared in Table 2.

TABLE 2.

Comparison of K_{Si} Values.

Temp. °C.	Korber and Oelsen(37)	Hilty and Crafts(23)	Chipman and Gokcen(31)	Schenck and Wesener(29)	Bell(16)
1550°C	1.34×10^{-3}	1.6×10^{-3}	1.1×10^{-3}	1.74×10^{-3} (1540°C)	1.3×10^{-3}
1600°C	3.6×10^{-3}	3.0×10^{-3}	2.8×10^{-3}	3.8×10^{-3}	-

(d) Fe-Mn-Si-O Equilibrium.

When the equilibrium between molten iron and iron manganese silicate slags is considered the main reactions of interest are the silicon reaction (already considered in "C"), the manganese reaction and the manganese-silicon reaction. The equations for the latter two reactions, are,

$$\underline{Mn} + (FeO) = (MnO) + \underline{Fe}$$

$$\text{for which } K'_{Mn} = \frac{(\%MnO)}{[\%Mn].(\%FeO)}$$

$$\text{and } \underline{2Mn} + (SiO_2) = \underline{Si} + (2MnO).$$

If this reaction is carried out in the presence of solid silica, the equilibrium constant may be written,

$$\text{Log } K_{MnSi} = \frac{[\%Si](\%MnO)^2}{[\%Mn]^2}$$

for which Korber and Oelsen(37) found $\log K_{MnSi} = \frac{9177}{T} - 4.757$. This gives values of 9.6×10^{-6} and 8.6×10^{-6} at 1550°C and 1600°C respectively. In the presence of silica, K'_{Mn} differs from K_{Mn}, as silica affects the activities of FeO and MnO to different degrees. Korber and Oelsen found that K'_{Mn} was considerably higher with these slags than with simple FeO-MnO slags. They also observed that K'_{Mn} was independent of FeO/MnO ratio but decreased with rise of temperature.

Although there was a considerable scatter in their results, a large enough number of experiments was carried out to justify expressing the relationship between temperature and the mean value of K'_{Mn} in the form,

$$\text{Log } K'_{Mn} = \frac{7919}{T} - 3.172$$

which gives K'_{Mn} values of 15.5 and 11.7 at 1550°C and 1600°C respectively.

Although Schenck and Wiesner(20) determined K'_{Mn} for silica saturated FeO-MnO-SiO_2 slags, the actual numerical data are not given, the results having instead been expressed in terms of γ_{MnO}. The latter was derived from the equation,

$$K_{Mn} = K'_{Mn} \frac{\gamma_{MnO}}{\gamma_{FeO}}$$

K'_{Mn} has also been determined by Bell(16) from the results of slag-metal experiments in silica crucibles at 1550°C. Although the number of experiments, carried out, was small, the scatter of the results was far less than that obtained by Korber and Oelsen(37) so that a greater measure of reliability may be placed on his results. The mean value of K'_{Mn} at 1550°C was 15.5. The reduced scatter may be attributed to the better control of temperature, the longer time of the experiments and the more careful chemical analysis of the metal and slag sample.

Very little work has been carried out on slag-metal equilibria using FeO-MnO-SiO_2 slags not saturated with silica. Such experiments must be conducted in a refractory crucible, such as, MgO or Al_2O_3 and these oxides inevitably enter the slag, making interpretation of the results obtained less certain. The earliest work in this direction was that of Krings and Schackmann(40) who added varying amounts of silica to slag metal melts carried out in Al_2O_3 or MgO crucibles. More accurate work was carried out by Bell, Murad and Carter (15,16), who

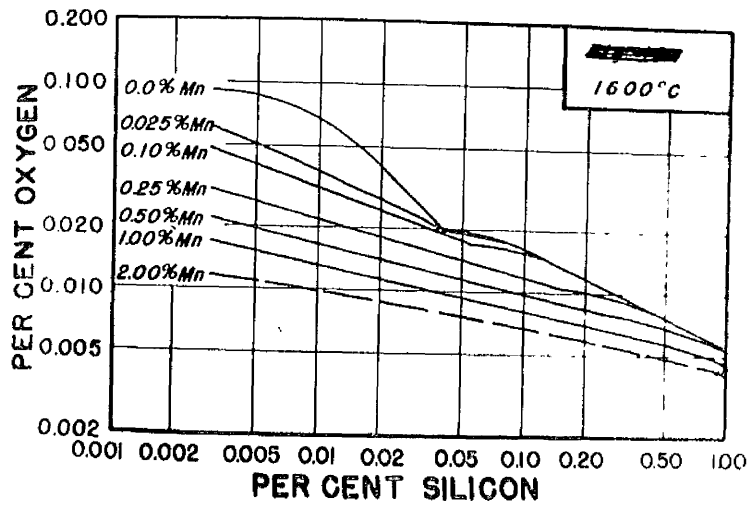


FIG. 11. SOLUBILITY OF OXYGEN IN LIQUID IRON CONTAINING SILICON AND MANGANESE AT 1600°C (HILTY & CRAFTS)[23].

used the values of K'_{Mn} obtained to calculate activities of MnO. This work was only carried out at 1550°C.

The work of Hilty and Crafts(23) in this field discussed in the previous section was unsuccessful in that they were unable to obtain satisfactory slag samples. Their metal analysis data were used to show graphically the relation between silicon, oxygen and manganese in the metal at 1600°C. Their curves shown in Fig.11, show similar inflexions to those obtained in the investigation of the Si-O equilibrium, which again, are thermodynamically unsound. The inflexions, however, disappear with higher manganese additions.

In the reaction

$$2\underline{Mn} + (SiO_2) = (2MnO) + \underline{Si}$$

a_{SiO_2} is constant and equal to unity for melts made in silica crucibles. At high manganese contents, the slag is almost pure manganese-silicate saturated with silica in which the activity of MnO will be approximately constant. Thus the equilibrium constant for the above reaction may be rewritten as,

$$[\%Si]/[\%Mn]$$

A plot of log Si against log Mn would be expected to give a linear relation with a slope of 0.5. This was found by Korber and Oelsen(37) but the results of Hilty and Crafts(23) differ considerably as shown in Fig.12.

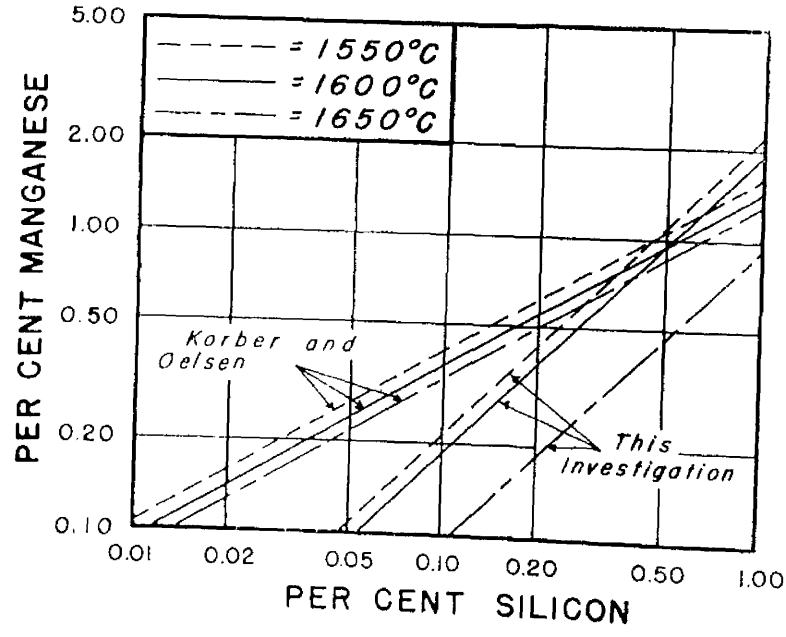


FIG. 12. MANGANESE AND SILICON CONTENTS OF LIQUID IRON IN EQUILIBRIUM WITH SILICA-SATURATED SLAGS (HILTY & CRAFTS) (23).

["THIS INVESTIGATION" MEANS THE INVESTIGATION OF HILTY & CRAFTS]

CHAPTER 3.

EXPERIMENTAL TECHNIQUE.

EXPERIMENTAL TECHNIQUE.

(a) Choice of Crucible Material and the Making of Crucibles.

In high temperature slag-metal investigation, one of the most difficult problems confronted is the selection of a suitable crucible material. This must withstand high temperatures, possess good mechanical strength and be chemically inert to both slag and metal. Chemical inertness is the most difficult to attain since metal crucibles cannot be used in the presence of molten iron and all refractories so far used are attacked in varying degrees by slags containing iron oxide. Characteristic properties of the individual oxides available have been reviewed by Kirby(41).

Of the available oxide materials, MgO, Al_2O_3, BeO and SiO_2 appeared to be the most suitable. SiO_2 was used for experiments with SiO_2 saturated slags, but for slags not saturated with SiO_2, MgO was chosen, since the use of Al_2O_3 would lead to the formation of slags saturated with Al_2O_3 and the behaviour of BeO in slags is not clearly understood. BeO also has certain harmful toxic properties. The use of MgO crucible led to saturation with MgO, but the solubility of MgO in FeO-MnO-SiO_2 slags not saturated with SiO_2 is less than that of Al_2O_3(40) and it is believed that MgO would behave as neutral or weakly basic oxide in such slags, whereas Al_2O_3 would probably form aluminates with FeO and MnO, thereby introducing an additional complication into the interpretation of the slag-metal results. Magnesia crucibles were also more suitable since these enabled a direct comparison with previous work(9,15,16,20,23) to be made.

Magnesia crucible have been prepared by firing in an induction furnace round a graphite core(42,43) and hand ramming of a paste in a rotating furnace, the molten metal forming a cup against the inside wall of the crucible, thereby reducing slag attack(13,15,23). The former process gave crucibles which did not withstand slag attack. The latter method, although offering advantages in certain cases, has been found unsuitable when working with slag of low viscosity, such as iron-manganese silicate slags low in silica content. Attention was therefore paid to the technique of slip-casting. Although Al_2O_3 can be easily slip-cast using water as a suspending medium, magnesia due to its ease of hydration cannot be treated thus. Even when using undried alcohol, magnesia crucibles cracked during drying and firing. Therefore ethyl alcohol dried by the Grignard method was used as a suspending medium. Methanol and Ethanol were found equally satisfactory when properly dried. The crucibles are prepared by pouring the suspension into a plaster of Paris mould, the crucible being formed by adsorption of the suspending liquid by the plaster, leaving a layer of refractory on the plaster surface.

Preparation of plaster mould. Finely ground plaster of Paris was added gradually to water and lumps broken by hand until the mixture was of the consistency of thick cream. It was then poured into an iron mould made from a split tube. Prior to pouring of the plaster-suspension, the two halves of the split tube were smeared with vaseline

and clamped together. The brass former corresponded in size to the external dimensions of the crucible required, after allowing for shrinkage during drying and firing (approx. 15-20 percent in the case of MgO). The former was slightly tapered to allow for easy removal of the crucibles to be made. After the plaster had set, the former and iron mould were removed and the plaster mould allowed to air dry for 2-3 days before use. Several moulds were usually made at the one time to speed up crucible preparation. Figure 13 shows the clamped two halves of the mould, with the brass former in position, ready to receive plaster-suspension. Figure 13(a) shows the vertical cross-section of the plaster mould after removing the former and the iron mould.

Grinding of magnesia: Grinding for 40 hours in a rubber lined ball mill using magnesite balls to about 200 mesh was found necessary in order to obtain dense and compact crucibles after firing. The magnesia used contained about 0.5 per cent SiO_2, and was stored in an air-tight jar after grinding to avoid hydration.

Crucible preparation. Ground magnesia was added to dried alcohol to give a very viscous mixture almost the consistency of treacle. This was left in an air-tight jar overnight and stirred again in the morning. The slip was poured into the plaster mould and allowed to remain $\frac{1}{2}$ - 1 minute to give a crucible with a thick enough wall, generally $1\frac{1}{2}$ - $2\frac{1}{2}$ mm. after which the slip was poured off. The mould was gently rotated by hand during settling and pouring. The crucibles were allowed to stand

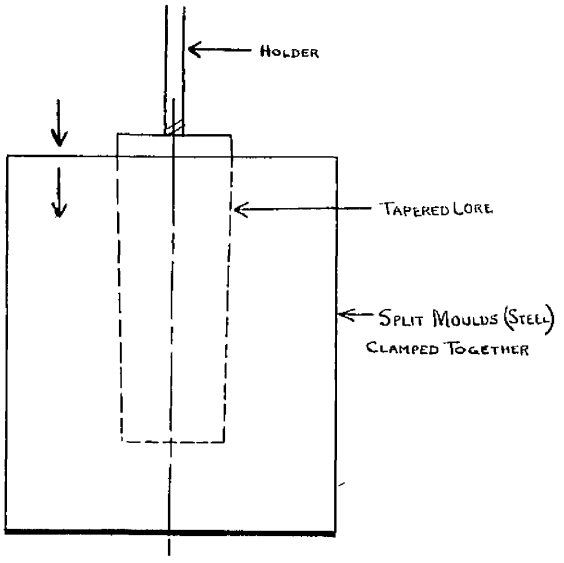


FIG. 13. PREPARATION OF PLASTER OF PARIS MOULD.

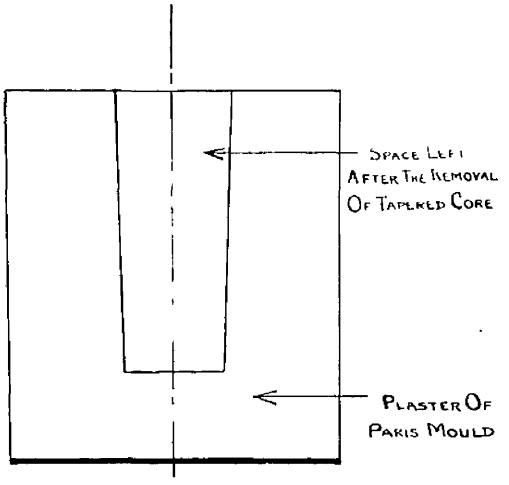


FIG. 13(a). VERTICAL CROSS-SECTION OF MOULD AFTER REMOVAL OF CORE.

for about 5 minutes in the plaster mould before removal. The time of standing increased with the number of crucibles made. After making three or four crucibles, the mould was left drying and other moulds were used. Magnesia crucibles do not shrink easily from the walls of the plaster moulds, but dusting the mould with French chalk before each crucible was cast made removal fairly easy. The crucibles which were very fragile after removal, were allowed to air-dry for about 2 days. The first batch was fired at 1650°C for 2-3 hours. During experiments with FeO-MnO slags, it was found that the MgO pick-up was 6-11.5 percent. A second batch fired at 1750°C for 3 hours, gave a pick-up of about 4 percent, and had a greenish translucent tinge due to recrystallization. Crucibles prepared by slip-casting followed by firing at 1750°C, proved extremely satisfactory and withstood the attack of FeO at 1600°C for 6 hours without failure. It seemed probable from their appearance that they could have withstood attack for much longer periods. Eight percent of the experiments made with the above crucibles were lost due to crucible failures. These failures did not originate from slag attack. It seemed probable after careful examination that minute hair line cracks could have developed during drying or firing which could not be detected before the runs, and that slag leaked through these cracks. Very careful handling during making, drying in a dry atmosphere and firing eliminated the trouble during the making of a third batch of crucibles.

The crucibles made were 2.3 inches in length, O.D. at top 1 in., at bottom 0.85 in., and I.D. 0.8 in.

(b) Materials Used in Melts.

Metal charge. Armco iron bars (C = 0.01 pct., Mn = 0.015 pct., P = 0.004 pct., Si = <0.002 pct., S = 0.020 pct.) were forged to a suitable diameter and machined to remove surface scale. Pieces approximately 2.5 in. in length were drilled into the form of crucibles to fit inside the magnesia or silica crucibles. Drilling was carried out.

(a) to remove segregates of inclusions which might occur near the axis of the bar,

(b) to enable the desired amount of slag to be placed inside the metal, thereby minimising slag-crucible attack during melting, at the beginning of the experiment. This avoids opening the system to the atmosphere for slag addition,

(c) to avoid damage to the combustion tube caused by scattering of oxide particles during addition of slag constituents.

Slag Constituents. Natural white silica sand was ground to about 100 mesh and repeatedly boiled in HCl acid and washed with distilled water. When it was acid free, it was ignited to about 1000°C for several hours to remove carbonaceous material. Sand prepared in this way contained more than 99.5 percent SiO_2.

Iron Oxide. Ferrous oxide was prepared by heating ferrous oxalate to 1000°C in an iron tube in vacuum for about 1½ hours, and quenching in water while still evacuated. The ferrous oxide obtained was spongy and black in appearance and contained more than 98 percent ferrous oxide, the remaining being ferric oxide.

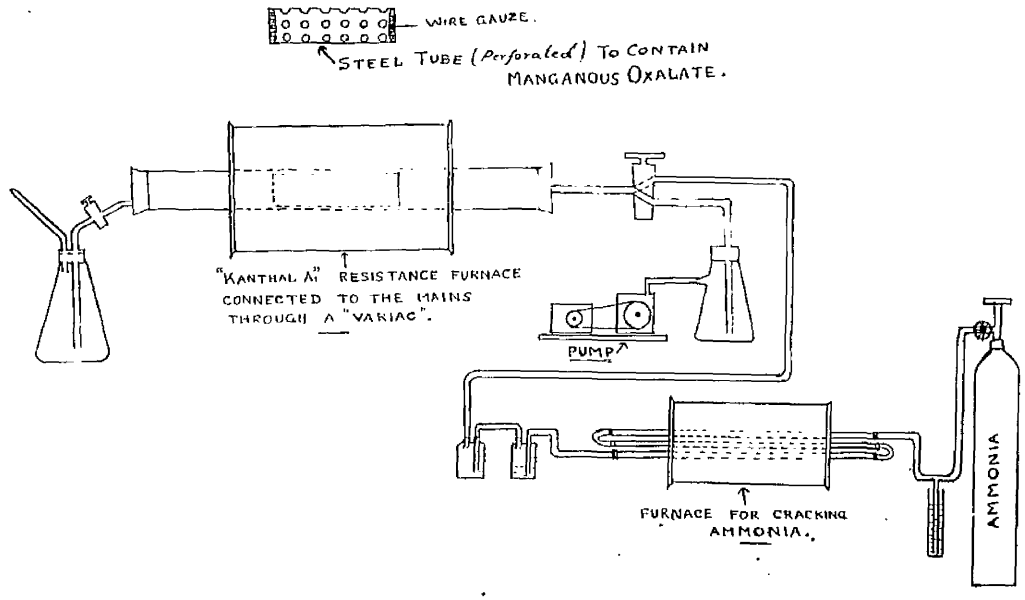


FIG. 14. APPARATUS USED TO PREPARE MANGANOUS OXIDE FROM MANGANOUS OXALATE.

Manganese Oxide. Manganese oxide was prepared by heating manganese oxalate in cracked ammonia or hydrogen (after evacuating) in an alumina boat or perforated steel tube, the temperature being slowly raised to about 1150°C. After holding for 1-1½ hours, cooling was carried out in the same atmosphere. The manganous oxide obtained was bright green and contained 99 percent MnO. The apparatus used is shown in Figure 14.

(c) Furnace and Apparatus.

Furnaces. Two furnaces were used for the slag-metal equilibrium work. A platinum wire wound resistance furnace was used for experiments in magnesia crucibles, and a molybdenum furnace for those carried out in silica crucibles, since the latter were too large to enter the tube of the platinum furnace.

The platinum furnace is shown in Figure 15, and is of conventional design. The mullite combustion tube, 1½ inche internal diameter x 36 inches long, was impermeable to gases up to the working temperature. Temperatures were measured by a platinum - 13 percent platinum-rhodium thermocouple protected by an 18 inches long alumina sheath which was inserted through the bottom bung, as shown in Figure 15. The E.M.F. generated by the couple was measured on a sensitive Tinsley Vernier Potentiometer. The thermocouple was standardised, using the melting points of gold (1063°C) and palladium (1554°C) and frequently checked against a standard couple. The accuracy of the calibration was confirmed during experimental runs when the melting of Armco iron

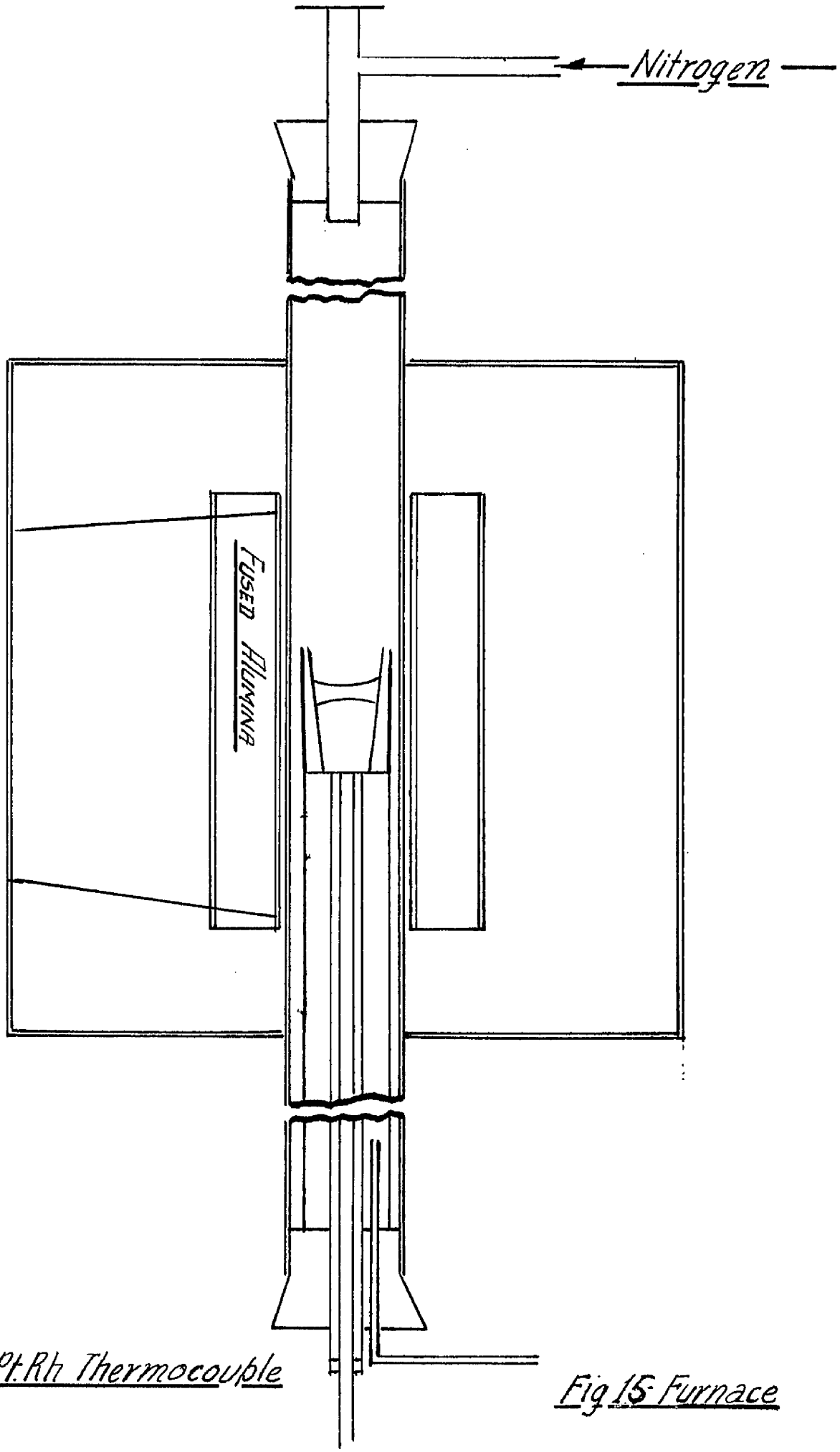


Fig 15 Furnace

agreed with the thermocouple reading within ± 3°C. The electrical input to the furnace was controlled by means of a 16 ampere variac autotransformer.

The molybdenum wire wound furnace used is shown in Figure 16. The winding was protected from oxidation by passing a cracked ammonia gas, and the outer shell of the furnace, with the exception of the glands through which the combustion tube was raised or lowered, was welded. The glands were screw-tightened after inserting an asbestos washer round the tube to seal the winding off from the outside atmosphere. The mullite furnace working tube was 36 inches long and 2 inches inside diameter.

The input to the furnace was controlled by a 40 ampere variac autotransformer.

Nitrogen supply. Commercial nitrogen, as supplied in cylinders, contains a small percentage of oxygen. This was removed by passing the nitrogen successively over copper gauze, steel wool and magnesium turnings, all being maintained at 600°C in a horizontal nichrome wound furnace. The nitrogen was finally dried by passing through sulphuric acid and magnesium perchlorate before passing to the experimental furnace.

Furnace Operation. An Armco-iron crucible (50-60 gms.) was weighed and the required amount of slag of the desired composition added. It was found after trial that for the magnesia crucibles used in these

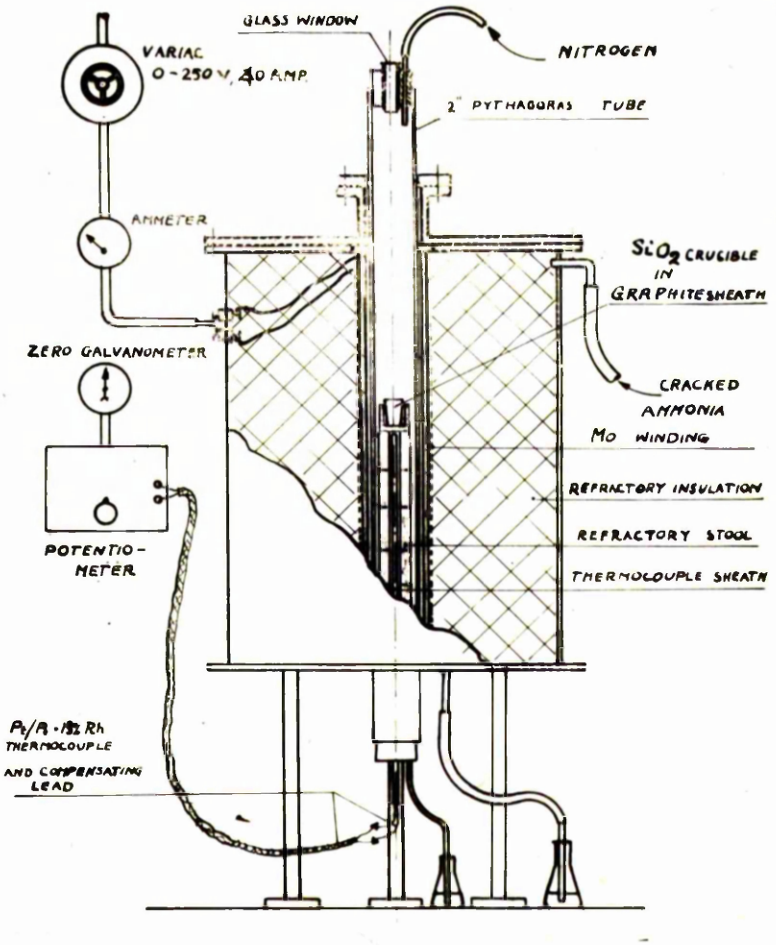


FIG. 16. SCHEMATIC DRAWING OF MOLYBDENUM FURNACE.

experiments, 10 gms. of slag was enough to give a slag layer about 5-6 mm. deep which was satisfactory for sampling. The crucible and slag were placed inside the magnesia crucible which was in turn placed inside a thin walled alumina crucible, and introduced into the cold furnace, in the centre of the "hot zone". The outer alumina crucible served two purposes;

(a) The magnesia crucible would tend to fuse with the mullite furnace tube at the reaction temperature if they came into contact, thereby resulting in loss of the mullite tube. Alumina does not react in this fashion with mullite and can be used safely in contact with magnesia, since the only compound likely to be formed, spinel, is of very high melting point.

(b) In the case of crucible failure, the alumina crucible might hold any escaping slag, thereby providing an additional protection for the furnace tube, stools and thermocouple sheath.

Nitrogen was passed through the furnace for about 5 minutes before heating commenced, and this atmosphere was maintained throughout the experiment. The melting point of iron was reached in about 7 hours, and the desired working temperature of 1550°C to 1600°C was reached in a further 20-60 minutes respectively. According to previous workers on slag-metal equilibria (9,15,16,19,21,37,40), a time of 30 minutes - 1 hour is quite sufficient to reach equilibrium between molten-iron and FeO-MnO-SiO_2 slags. This is in agreement with the present results, where varying the experimental time from 30 minutes to 2 hours did not

materially affect the results obtained, as shown in Table 8.

TABLE 8.

Effect of Time on Equilibrium.

Run	Temperature	Time	K_{Mn}
6	1600°C	0 hr. 22 min.	2.00
13	"	0 hr. 35 min.	3.0
7	"	0 hr. 45 min.	3.4
11	"	0 hr. 46 min.	3.6
12	"	1 hr. 50 min.	3.33
47	1550°C	0 hr. 40 min.	4.12
46	"	1 hr. 30 min.	4.33
45	"	1 hr. 40 min.	4.55
48	"	1 hr. 45 min.	4.17

The direction of approach to equilibrium also did not affect the results.

After holding the slag and metal for the required time, slag and metal samples were taken. Slag samples were obtained by inserting an Armco-iron rod into the molten slag, which chilled instantaneously round the bar; care was taken to avoid the entry of the rod into the molten metal. Metal was sampled by a modification of the method of Taylor(13),

a silica tube being used instead of a silica tube and copper block. The metal was sucked into the silica tube where it solidified almost immediately. The tube was quenched in cold water on withdrawal from the furnace.

Finally, a known amount of a silicon-manganese deoxidiser was added to the molten metal remaining, and a further metal sample drawn within 1-2 minutes. When the metal charge was sufficient, a second deoxidised sample was drawn 5-6 minutes after adding the deoxidiser. The temperature was maintained constant during sampling.

Resistance of the crucibles to slag and metal attack is depicted in Figure 17, which shows the crucible after melting.

Experiments in Silica Crucibles. These were carried out in the molybdenum wound furnace. The silica crucibles were made from silica tubing 1.5 in. external diameter and 0.25 in. wall thickness, to which a flat end was fused using silica sheet of the same thickness. In order to avoid excessive attack on the crucibles during experiments, the slags added contained 30-40 percent SiO_2. With such additions it was possible to carry out experiments successfully at 1600°C for at least one and a half hours.

The silica crucibles were placed inside a thin walled graphite crucible (wall thickness 1 mm.). A hole was drilled in the bottom of the graphite crucible into which was placed a ring type alumina sleeve to protect the alumina thermo-couple sheath, as shown in Fig.18. The silica crucibles were larger in diameter than the magnesia crucible

FIG. 17. MAGNESIA CRUCIBLES AFTER EXPERIMENTAL RUNS.

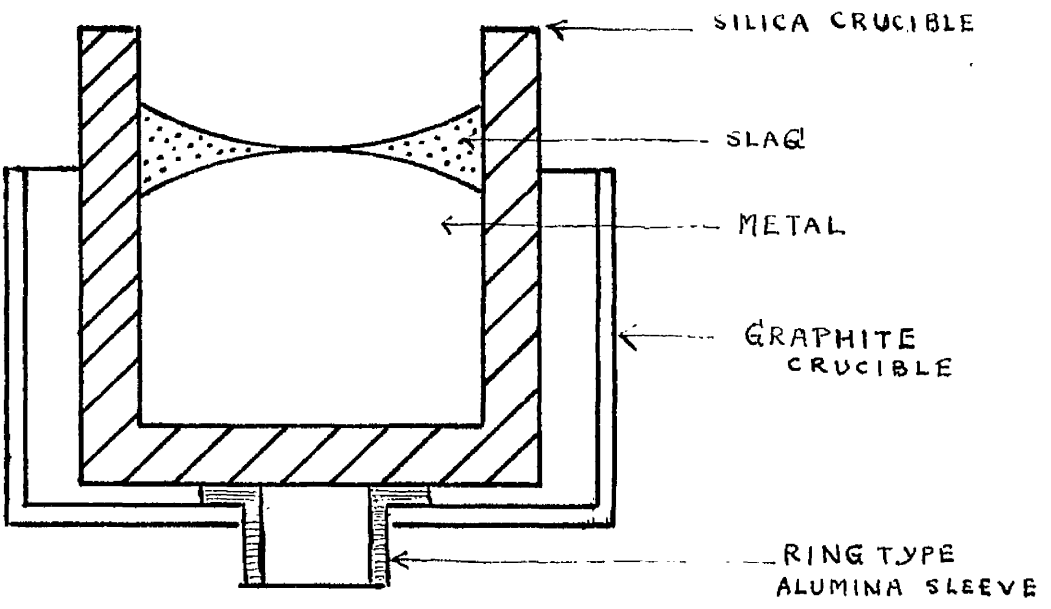


FIG. 18. VERTICAL CROSS SECTION SHOWING THE SILICA CRUCIBLE ASSEMBLY.

and could take larger charges of metal (80-100 gms.) and slag (20 gms).

Slag and metal sampling and deoxidation practice were the same as described before.

Determination of Hot Zone. The hot zone of each furnace was determined by inserting two standardised thermocouples simultaneously into the furnace tube, one from the top and the other from below through a thermocouple sheath. The top thermocouple was suspended from the arm of a calibrated vertical scale stand. The arm could move up and down on the scale and the distance through which the thermocouple was raised or lowered was recorded. The location of the uniform range of the hot zone was indicated when both couples agreed in temperature reading.

(d) Analysis of Slag and Metal.

Slag Analysis. Slag samples were finely ground and freed from entrapped iron with a magnet. During this operation, it was found that if the magnet was held close to the powder, a portion, amounting to about 15-20 percent of the total slag weight could be readily attracted and separated. The tendency was more marked with slags low in SiO_2 in which the proportion of magnetite is higher. This fraction was separated before analysis in runs carried out at 1575°C and it is probable that a slight discrepancy in the results obtained at this temperature is due to this fact.

The slags were analysed for total iron, ferrous oxide, manganous oxide, magnesia and silica. Total iron was determined by reduction with $SnCl_2$, followed by titration with standard $K_2Cr_2O_7$ solution, using sodium-diphenylamine sulphonate as indicator. Ferrous oxide was determined by dissolving a sample of slag in HCl acid in an inert atmosphere of CO_2, cooling in the same atmosphere and titrating rapidly against $K_2Cr_2O_7$ solution. Ferric oxide was obtained by difference.

Manganese oxide in the slag was determined by solution in dilute HNO_3 using a few drops of HF acid to aid solution. The solution was oxidised by sodium bismuthate, titrated with Ferrous ammonium sulphate and back titrated with $KMnO_4$ solution.

Silica was determined by the B.S.I. method(44). In this method, the slag sample was decomposed by HCl acid, oxidised by HNO_3, and the silica dehydrated by fuming with $HClO_4$. The silica precipitate was ignited and treated with HF and H_2SO_4.

Magnesia was determined by dissolving the slag sample in HCl acid, oxidising with H_2O_2 and then treating the solution with bromine followed by neutralisation by $CaCO_3$. The solution was filtered and titrated hot with NaOH in the presence of alcohol and nitrobenzene, using thymolphthalein as an indicator.

Metal Analysis. Metal samples were analysed for manganese, silicon and oxygen.

Manganese. An absorptiometric method(45) was used for the determination of manganese. The manganese was oxidised by periodate to permanganic acid and the light absorption of the coloured solution was compared with that of the same solution after decolourising with sodium nitrite, using a mercury vapour lamp, an Ilford spectrum yellow-green filter No.605 and heat filter calorex H.503.

Silicon. The silicon content of the iron was too low to be estimated by the gravimetric analytical procedure and an absorptiometric method(46) was used. Although 0.05 - 2.0% silicon can be estimated satisfactorily by the Gentry and Sherrington(47) absorptiometric method, it was found necessary to modify the method to obtain reproducible results at very low silicon concentrations, i.e., less than about 0.05% silicon. The general principle of both the original and the modified method is the same. The only essential difference is the final reduction of silico-molybdate to molybdenum blue which is carried out by the stannous chloride in the original method for the higher silicon range and by ferrous sulphate in the presence of oxalic acid in the lower range. An accuracy of ±0.002% has been claimed for silicon contents up to 0.01%.

Dall(16) found that if reagents, especially potassium permanganate solution, were kept in glass bottles for some time, the blank steadily increased with time, whereas a new solution would give a reproducible blank. In the present work, reagents, such as, $KMnO_4$ solution,

Ammonium Molybdate solution and Ferrous ammonium sulphate solutions, were all kept in wax bottles. By taking this precaution no difficulty was experienced in obtaining results reproducible within ±0.001%. All estimations were made in duplicate and in some cases in triplicate.

Oxygen. The oxygen content of the iron was determined by "Vacuum Fusion Method". The apparatus used was similar to that used by Murad(48) and is illustrated in Figure 19. The weight of metal samples varied from 0.8 gms. to 1.8 gms. depending on the probable oxygen content. The samples were cleaned and an axial slit made to remove any inclusions which may have segregated along the axis of the specimen. Five to six samples were then introduced into the side arm "C" of the apparatus and the rotary pump switched on. This lowered the pressure in the system to 0.01 mm. Hg. A four stage Hg-diffusion pump was then used to reduce the pressure in the translucent silica tube side of the system to less than 10^{-5} mm. Hg. The high frequency current was then switched on and the graphite crucible degassed for about 4 hours at 2000°C during which time the pressure in the furnace tube increased to about 10^{-2} mm. Hg. The furnace temperature was then adjusted to 1950°C when the pressure once more fell below 10^{-5} mm. Hg. When pressure conditions were steady, a gas blank for the apparatus over a period of 20-30 minutes was withdrawn using a "Toepler pump". The gas sample was analysed for "CO" in a "Sleigh analyser". The metal samples were then dropped and gas samples withdrawn and analysed in the same manner.

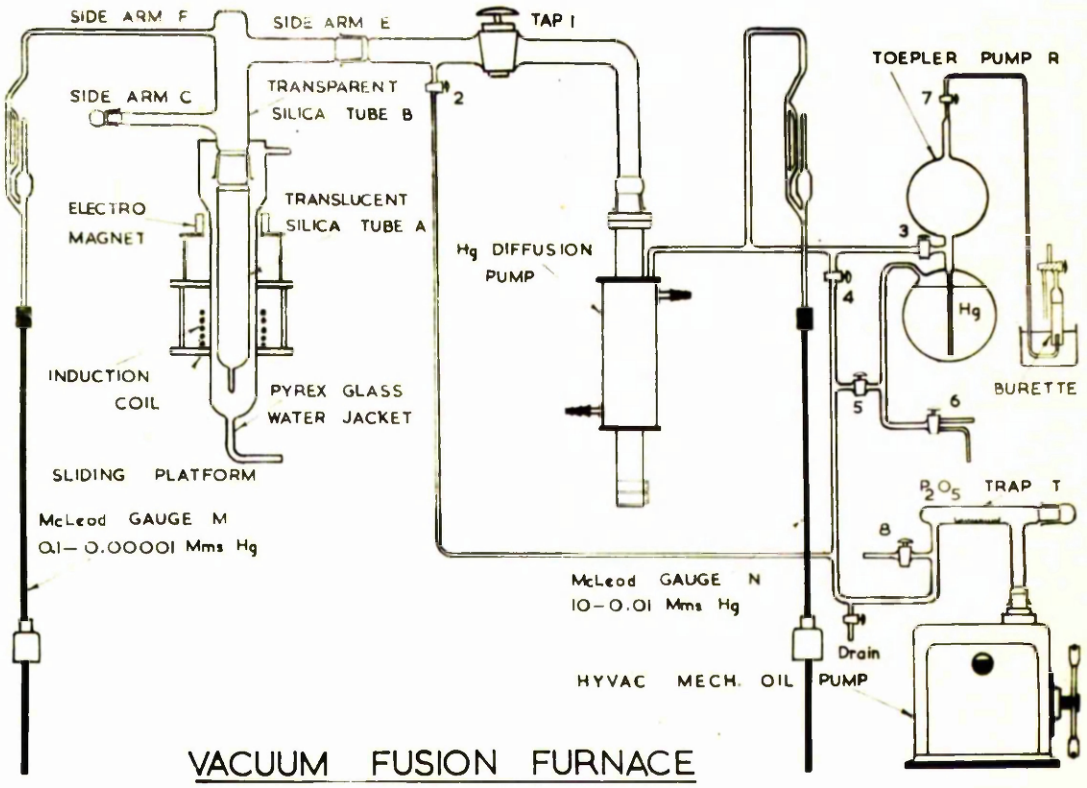


FIG. 19. VACUUM FUSION APPARATUS USED FOR OXYGEN DETERMINATION.

The apparatus was checked at intervals against standard samples supplied by the National Physical Laboratory and the British Iron and Steel Research Association. Results were always reproducible within ±0.001% oxygen.

CHAPTER 4.

EXPERIMENTAL RESULTS.

EXPERIMENTAL RESULTS.

Sixty-three experimental runs were carried out, of which fifty-one were successful, the remainder being lost due to crucible failure and to furnace failure. Slag and metal analyses of successful runs are summarised in Table No.4. Slag analysis have been expressed both as weight percentage and mole-fractions. Most of the runs were carried out at 1600°C to obtain the effect of temperature. A small number of melts were carried out at 1550°C and 1575°C to determine K_{Mn} and three runs were carried out in silica crucibles at 1550°C in order to get a direct comparison with Bell(16) of K'_{Mn} values at this temperature under silica saturated slags.

TABLE 4.

Run	Metal Analysis % Mn	O	Si	Slag Analysis Weight %. FeO	Fe_2O_3	ΣFeO	MnO	SiO_2	MgO	Slag (Mole Fraction) ΣFeO	MnO	SiO_2	MgO	K'_{Mn}
1600°C Iron oxide slags in MgO crucibles.														
1	-	.189	*	N.D.	N.D.	91.0	N.D.	tr.	8.9	.852	-	-	.147	-
2	-	.198	-	N.D.	N.D.	91.2	N.D.	tr.	8.8	.854	-	-	.147	-
3	-	.195	-	N.D.	N.D.	91.8	N.D.	tr.	8.2.	.863	-	-	.138	-
4	-	.203	-	N.D.	N.D.	94.4	N.D.	tr.	5.5	.907	-	-	.094	-
1600°C FeO-MnO slags. No SiO_2 addition MgO crucibles.														
5	.028	.17	.032	88.9	3.5	87.0	7.0	0.6	5.2	.89	.069	.007	.089	2.89
6	.03	.178	.011	85.4	2.7	87.3	7.5	0.5	4.8	.899	.073	.006	.092	2.98
7	.028	.18	.011	80.1	3.2	83.9	7.9	0.4	7.4	.791	.076	.005	.126	3.4
8	.015	.168	.001	75.9	7.2	81.5	12.4	0.5	4.3	.792	.123	.005	.075	3.37
9	.055	.172	.001	N.D.	N.D.	79.6	13.7	0.4	6.4	.80	.140	.005	.115	3.1
10	.068	.148	.0025	70.2	4.2	74.0	13.9	0.5	11.5	.678	.129	.006	.188	3.12
11	.073	.16	.002	68.0	7.4	74.6	20.9	0.5	4.1	.719	.204	.006	.070	3.6
12	.10	.147	.001	65.5	7.0	71.8	24.1	0.2	3.0	.705	.24	.003	.053	3.39
13	.129	.143	.001	67.7	5.1	70.5	25.1	0.1	4.0	.68	.246	.002	.069	3.0
14	.17	.141	.0025	N.D.	N.D.	62.1	33.1	0.5	4.3	.593	.322	.005	.074	3.13
1650°C FeO-MnO-SiO_2 slags. MgO Crucibles.														
15	.038	.171	.001	62.3	7.5	70.7	20.4	3.2	5.9	.67	.196	.036	.100	3.1
16	.036	.137	.0025	54.6	7.4	62.9	25.5	4.1	7.5	.538	.242	.046	.124	4.2
17	.045	.168	.001	65.9	7.5	74.2	12.8	5.6	8.0	.686	.22	.062	.132	3.8
18	.069	.152	.0015	57.4	4.2	62.1	23.2	7.1	7.7	.576	.218	.078	.127	4.2
19	.080	.169	.001	55.1	4.2	60.8	25.3	7.3	7.1	.565	.241	.09	.117	4.6
20	.030	.121	.002	58.9	4.3	63.7	20.8	7.8	7.8	.584	.195	.087	.128	4.1
21	.099	.119	.002	46.1	3.9	50.4	31.9	11.1	9.8	.448	.279	.113	.155	6.2
22	.160	.106	.002	39.7	3.2	42.6	37.9	13.3	6.0	.396	.357	.147	.10	5.55
23	.113	.109	.001	38.1	3.6	42.1	29.9	15.0	13.1	.377	.267	.158	.20	6.3
24	.135	.114	.0022	34.9	3.5	38.8	32.3	15.9	13.8	.338	.285	.156	.22	6.2

TABLE 4.(Continued).

Run	Metal Analysis %			Slag Analysis Weight %						Slag(Mole Fraction)				K'_{Mn}
	Mn	O	Si	FeO	Fe_2O_3	ΣFeO	MnO	SiO_2	MgO	ΣFeO	MnO	SiO_2	MgO	
25	.14	.106	.0022	31.7	2.6	34.6	34.8	17.3	13.0	.30	.31	.385	.201	7.2
26	.063	.111	.002	33.5	2.3	36.0	24.5	20.2	18.3	.31	.211	.205	.276	8.2
27	.003	.104	.003	33.3	2.5	36.0	25.7	20.4	18.0	.32	.22	.21	.26	7.7
28	.220	.078	.003	24.5	1.6	25.9	39.2	22.8	12.7	.226	.357	.23	.193	6.99
29	.072	.123	.0025	32.5	3.0	36.0	21.5	22.4	20.0	.30	.18	.223	.30	8.3
30	.142	.058	.009	24.0	2.3	26.5	32.1	23.4	17.6	.233	.277	.238	.266	8.5
31	.22	.051	.001	14.2	1.8	16.2	38.4	27.3	22.9	.151	.274	.265	.338	9.4
32	.15	.046	.014	14.3	1.6	16.1	31.2	32.2	19.9	.134	.263	.321	.282	10.7
1600°C Silica-saturated FeO-MnO-SiO_2 slags. SiO_2 crucibles.														
33	.058	.062	.006	N.D.	N.D.	38.2	18.1	51.7	-	.274	.166	.55	-	12.45
34	.07	.046	.013	N.D.	N.D.	25.2	24.6	50.8	-	.229	.228	.543	-	14.07
35	.064	.036	.026	N.D.	N.D.	23.4	26.3	50.3	-	.232	.242	.546	-	13.33
36	.16	.08	.082	N.D.	N.D.	15.7	34.1	50.3	-	.142	.313	.545	-	13.38
37	.145	.035	.025	N.D.	N.D.	13.0	34.5	48.4	-	.161	.315	.523	-	13.21
38	.268	.028	.034	N.D.	N.D.	13.0	36.9	50.1	-	.118	.339	.542	-	13.6
39	.31	.0272	.093	N.D.	N.D.	9.4	39.0	51.6	-	.087	.357	.553	-	13.45
1575°C. FeO-MnO slags. No SiO_2 addition. MgO crucibles.														
40	.049	.143	tr.	77.4	3.6	80.6	12.9	0.35	5.2	.78	.126	.004	.09	3.99
41	.054	.151	tr.	78.6	4.6	77.8	16.3	0.41	4.9	.75	.16	.005	.084	3.9
42	.070	.147	tr.	71.1	4.2	74.9	20.3	.35	4.0	.78	.20	.004	.069	3.87
43	.063	.14	tr.	67.4	4.4	71.3	23.4	.46	4.2	.695	.227	.005	.072	3.95
44	.096	.13	tr.	65.9	3.6	69.1	25.0	.47	4.8	.67	.245	.005	.083	3.77

TABLE 4.(Continued).

Run	Metal Analysis % Mn	O	Si	Slag Analysis Weight % FeO	Fe_2O_3	ΣFeO	MnO	SiO_2	MgO	Slag(Mole Fraction) ΣFeO	MnO	SiO_2	MgO	E'_{Mn}
1550°C. FeO-MnO slags. No SiO_2 addition. MgO Crucibles.														
45	.022	.162	tr.	80.8	6.6	88.1	8.8	.39	3.4	.85	.086	.005	.059	4.55
46	.027	N.D.	tr.	N.D.	N.D.	83.2	9.9	1.1	5.52	.798	.096	.012	.094	4.38
47	.05	N.D.	tr.	N.D.	N.D.	85.3	10.5	.52	3.1	.84	.105	.006	.054	4.12
48	.055	.142	tr.	N.D.	N.D.	77.0	17.7	.44	4.7	.741	.172	.005	.081	4.17
1550°C. Silica-saturated FeO-MnO-SiO_2 slags. SiO_2 crucibles.														
49	.09	N.D.	N.D.	N.D.	N.D.	21.3	30.3	48.6	-	.193	.279	.528	-	15.8
50	.128	N.D.	N.D.	N.D.	N.D.	17.3	34.1	48.6	-	.157	.314	.529	-	15.99
51	.242	N.D.	N.D.	N.D.	N.D.	10.4	40.3	49.2	-	.094	.371	.535	-	16.07

CHAPTER 5.

EQUILIBRIA WITH METAL OXIDE SLAGS - NO SILICA ADDITIONS.

EQUILIBRIA WITH

(1) Solubility of oxygen in molten iron.

Runs 1-4 were carried out in magnesia crucibles of very low silica content at 1600°C, without any addition of MnO or SiO_2. The final silica content of the slags was less than 0.05 percent and insufficient

Runs 5-14 were carried out either by adding MnO to the slag constituents or manganese to the metal so that the manganese equilibrium could be approached from both directions. The mole fractions of MgO and MnO varied up to 0.188 and 0.322 respectively. Assuming that within these limits FeO, MgO and MnO form an ideal solution, the mean solubility of oxygen in iron at 1600°C under a pure iron oxide slag, as indicated in Table No.5, is 0.22 per cent. This value is in reasonable agreement with that calculated from the equation

$$\text{Log } \%\,O = -\frac{6320}{T} + 2.734$$

given by Chipman et al(12,13,20), viz., 0.23% at 1600°C.

Similar data obtained at 1575°C and 1550°C are shown in Table No.6 and yield mean values for the oxygen solubilities at these tempera-tures of 0.20 and 0.19 respectively. The latter figure is the same as that obtained by Ball(16) at 1550°C.

TABLE 5.

Temperature 1600°C.

Run	%O	Slag (mole fraction) (ΣFeO)	(MnO)	(MgO)	O Solubility = %O / N_{FeO}	K_{Mn}
1	0.189	0.852	-	0.147	0.222	-
2	0.193	0.854	-	0.147	0.226	-
3	0.195	0.863	-	0.130	0.226	-
4	0.203	0.907	-	0.094	0.224	-
5	0.17	0.83	0.068	0.089	0.205	2.80
6	0.173	0.839	0.073	0.082	0.207	2.9
7	0.18	0.791	0.076	0.126	0.226	3.4
8	0.168	0.792	0.123	0.075	0.212	3.37
9	0.172	0.80	0.14	0.115	0.215	3.1
10	0.148	0.678	0.129	0.188	0.218	3.12
11	0.16	0.719	0.204	0.070	0.223	3.6
12	0.147	0.705	0.24	0.053	0.209	3.33
13	0.143	0.68	0.246	0.069	0.210	3.0
14	0.141	0.593	0.322	0.074	0.236	3.13

TABLE 6.

Temperature 1550°C.

Run	O%	Slag (mole fraction) Σ FeO	MnO	MgO	O Solubility = $\frac{\%O}{\Sigma FeO}$	K_{Mn}
45	0.162	0.85	0.036	0.059	0.19	4.55
46	N.D.	0.798	0.096	0.004	-	4.36
47	N.D.	0.84	0.105	0.054	-	4.12
48	0.141	0.741	0.172	0.031	0.19	4.17

Temperature 1575°C.

40	0.143	0.78	0.126	0.09	0.185	3.99
41	0.151	0.75	0.160	0.034	0.20	3.90
42	0.147	0.73	0.20	0.069	0.20	3.87
43	0.14	0.695	0.227	0.072	0.20	3.95
44	0.13	0.67	0.245	0.083	0.20	3.77

The foregoing figures for oxygen solubilities are also in good agreement with the results of Chipman et al(12,13,20), and Darken and Gurry(2a) but are considerably lower than the values given by Herty and Gaines(8) and Körber and Oelsen(9). The present results are compared with those of Chipman in Fig.20. Over the range from 1550°C to 1600°C, the relationship between oxygen solubility and temperature is approximately linear.

It will be noted in a consideration of the oxygen solubilities given in Table 5, that the values obtained using FeO-MnO-MgO slags are slightly lower than those given by FeO-MgO slags. The discrepancy may arise from a slight lowering of the activity of FeO in the presence of MnO as has been suggested by Turkdogan and Pearson(49) and Darken(50) who stated this may be due to the formation of ferrites. It is, however, within the expected experimental error and no firm conclusion can be drawn on this point.

(11) K_{Mn} under oxide slags.

Values of K_{Mn} obtained with simple oxide slags are shown in Tables 5 and 6. The mean values for 1600°C, 1575°C and 1550°C are 3.2, 3.9 and 4.2 respectively. These values are compared with those of other workers in Table 7.

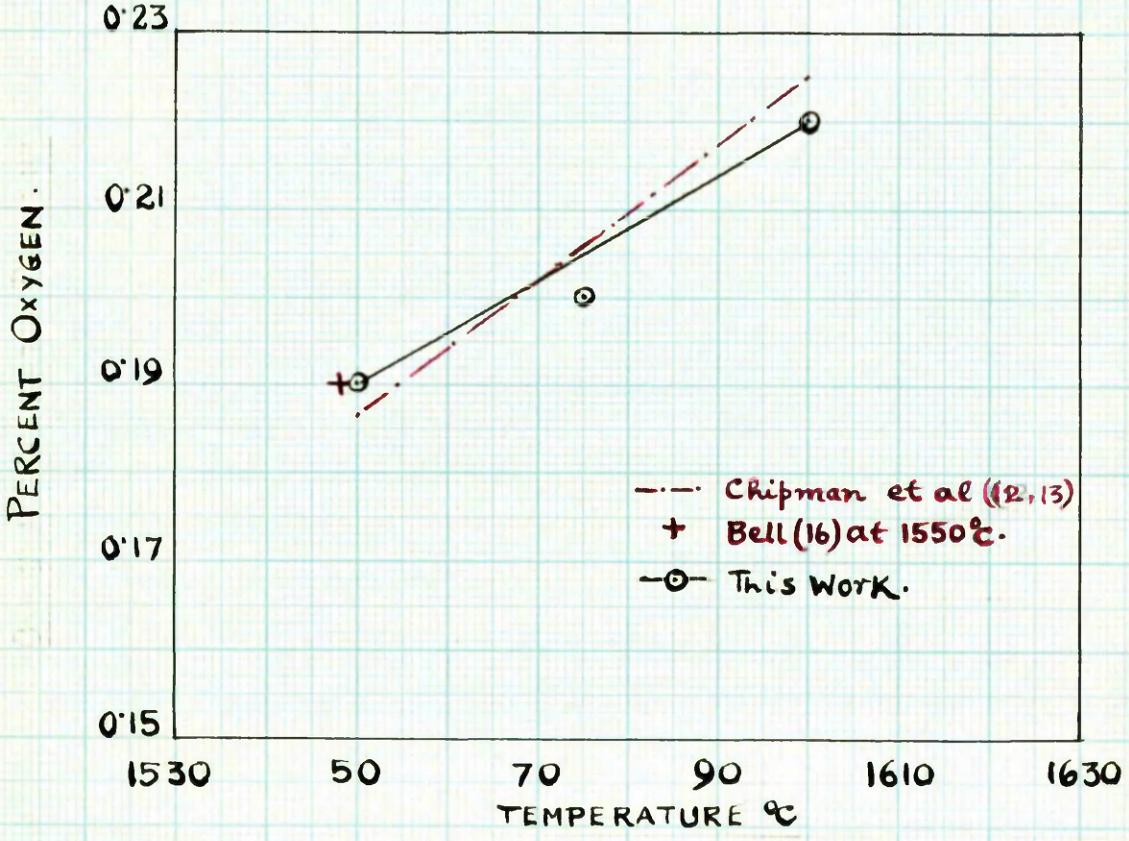


FIG. 20. EFFECT OF TEMPERATURE ON THE SOLUBILITY OF OXYGEN IN LIQUID IRON.

TABLE 7.

Comparison of Values of K_{Mn}.

Temp. °C.	This Work.	Bell (16)	Körber and Oelsen (9)	Chipman Gero and Winkler (20)	Turkdogan and Pearson. (22)	Krings and Schackmann (19)	Schenck Schmahl Bisswo (17)
1550	4.2	36	2.5	3.8	4.25	3.1±0.5	6.3
1575	3.9	"	-	3.42	3.7	-	5.8
1600	3.2	-	2.0	3.1	3.3	"	5.0

The lower values obtained by Körber and Oelsen(9) and Krings and Schackmann(19) and the higher oxygen solubilities which they also obtained suggest that the temperatures measured were too low. It is also probable that the time allowed for the reactions to reach equilibrium was insufficient. It should also be noted in the case of Krings and Schackmann(19) that some of their slag compositions correspond to the solid state at the working temperature of 1550°C - 1560°C. Values of log K_{Mn} obtained from the present experiments are plotted against $\frac{1}{T}$ in figure 21, which also shows the line given by Chipman, Gero and Winkler(20), and the line determined statistically from the latter's data by Turkdogan and Pearson(22). The present results are intermediate but agree better with the line given by Turkdogan and Pearson(22). The range of temperature in the present work is insufficient to decide whether the correct slope is the theoretically calculated one used by Chipman, Gero and Winkler(20) or the statistically determined one of Turkdogan and Pearson(22).

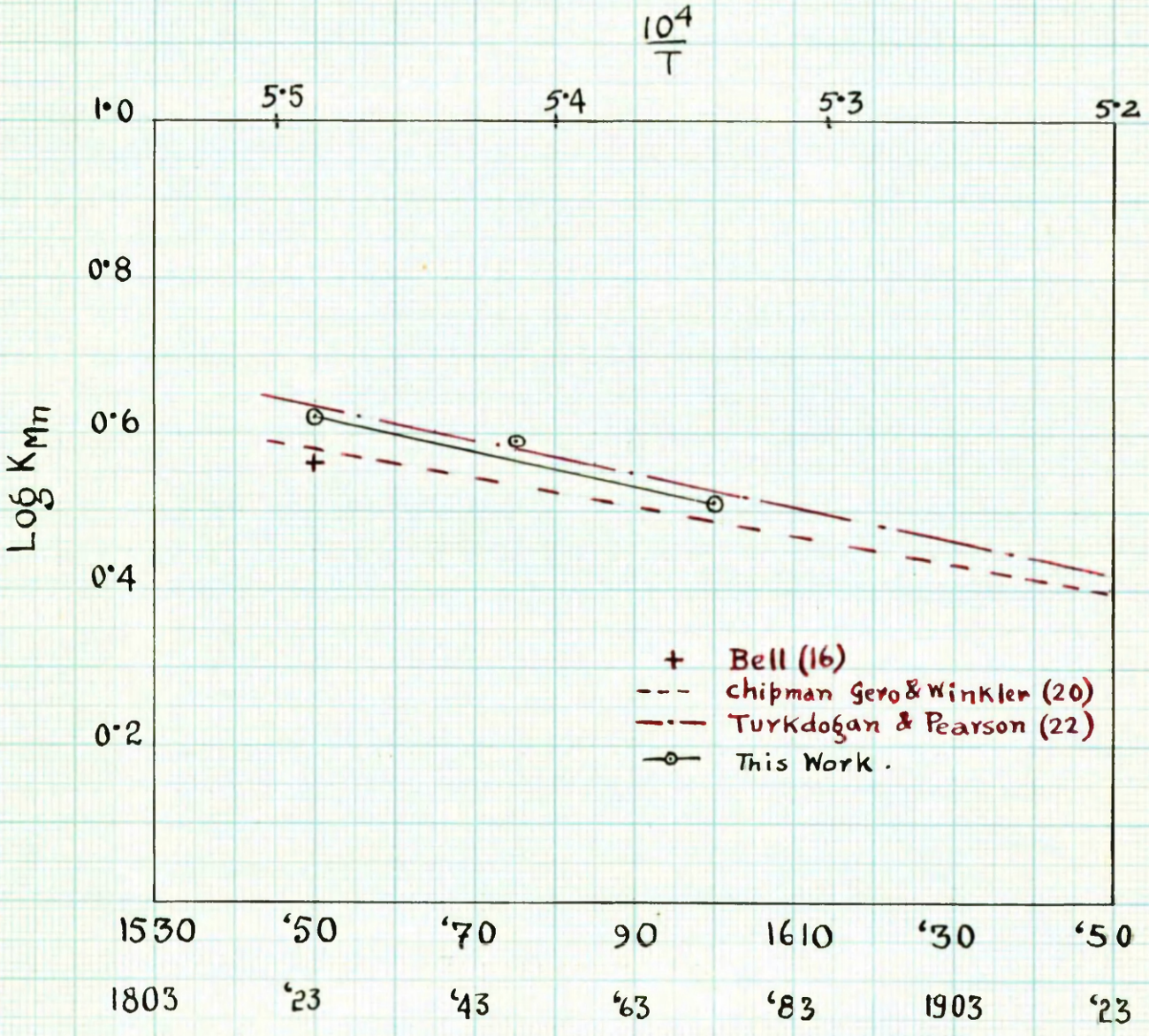


Fig 21 RELATIONSHIP BETWEEN Log K_m AND TEMPERATURE.

Although the point corresponding to 1575°C is shown in Fig.21, it has not been taken into account in representing the relationship between log K_{Mn} and temperature due to the doubt mentioned earlier as to the true analysis of the slag. It is probable that the deviation of this point from the line drawn is mainly due to this cause. The log K_{Mn} - temperature relationship can be expressed by the equation

$$\text{Log } K_{Mn} = \frac{7259}{T} - 3.359$$

The corresponding free energy change is,

$$\Delta G^\circ = -33170 + 15.36T$$

Considering the heat of fusion of MnO as 10,700 cals. as accepted by Chipman, Gero and Winkler(20) and which agrees well with the data of Schenck, Schmahl and Biswas(17), the free energy change for $MnO_{(s)} \rightleftharpoons MnO_{(\ell)}$ is $\Delta G^\circ = -10,700 + 5.2T$ (20).

Taking the free energy changes of $xFe_{(\ell)} + \frac{1}{2}O_{2(g)} \rightleftharpoons Fe_xO_{(\ell)}$; $\Delta G^\circ = -56,330 + 11.04T$(20) and $Mn_{(\ell)} \rightleftharpoons \underline{Mn}$; $\Delta G^\circ = -9.15T$(20), and assuming that Mn in dilute solution in molten iron obeys Henry's Law, then the free energy change for the reaction,

$\underline{Mn}_{(\ell)} + \frac{1}{2}O_{2(g)} \rightleftharpoons MnO_{(s)}$ is found to be

$\Delta G^\circ = -100,690 + 23.35T$(cals)

which is a reasonable value when compared with those given by other workers, as given below

(i) $Mn_{(\ell)} + \frac{1}{2}O_{2(g)} \rightleftharpoons MnO_{(s)}$; $\Delta G^\circ = -95,400 + 19.62T$ cals. (51)

(ii) $Mn_{(\ell)} + \frac{1}{2}O_{2(g)} \rightleftharpoons MnO_{(s)}$; $\Delta G^\circ = -97,000 + 21.4T$ cals. (20)

(iii) Effect of MgO on K_{Mn}.

From Table 5, it may be noted that the magnesia pick-up in the slag varied from MgO = 0.0527 to 0.188. Although impurities may have a noticeable effect on slag activities, the role of magnesia, within the above limits, in FeO-MnO slags, appears to be that of a diluent. Hence, the lower results of Körber and Oelsen(9) cannot be attributed to higher magnesia, as suggested by Turkdogan and Pearson(22), but more probably to an error in temperature measurement, as mentioned before.

(iv) Manganese-Oxygen Equilibrium in Liquid Iron under Pure Oxide Slags.

Fig.22 shows the manganese-oxygen relationship at 1600°C and 1550°C. The point at 0.13% manganese for 1550°C has been taken from the work of Bell(16). These curves represent the equilibria between manganese and oxygen in liquid iron under liquid FeO-MnO slags. Above approximately 0.17% and 0.13% manganese dissolved in liquid iron at 1600°C and 1550°C respectively, the equilibrium will be between a liquid iron-manganese-oxygen alloy and solid oxide slags. From the oxygen solubility values given in Table 5, it may be deduced that the concentration of manganese, as met with in these experiments, does not affect the activity coefficient of oxygen in liquid iron. This confirms the finding of Chipman(27), that $\epsilon_O^{Mn} = 0$ at 1% Mn.

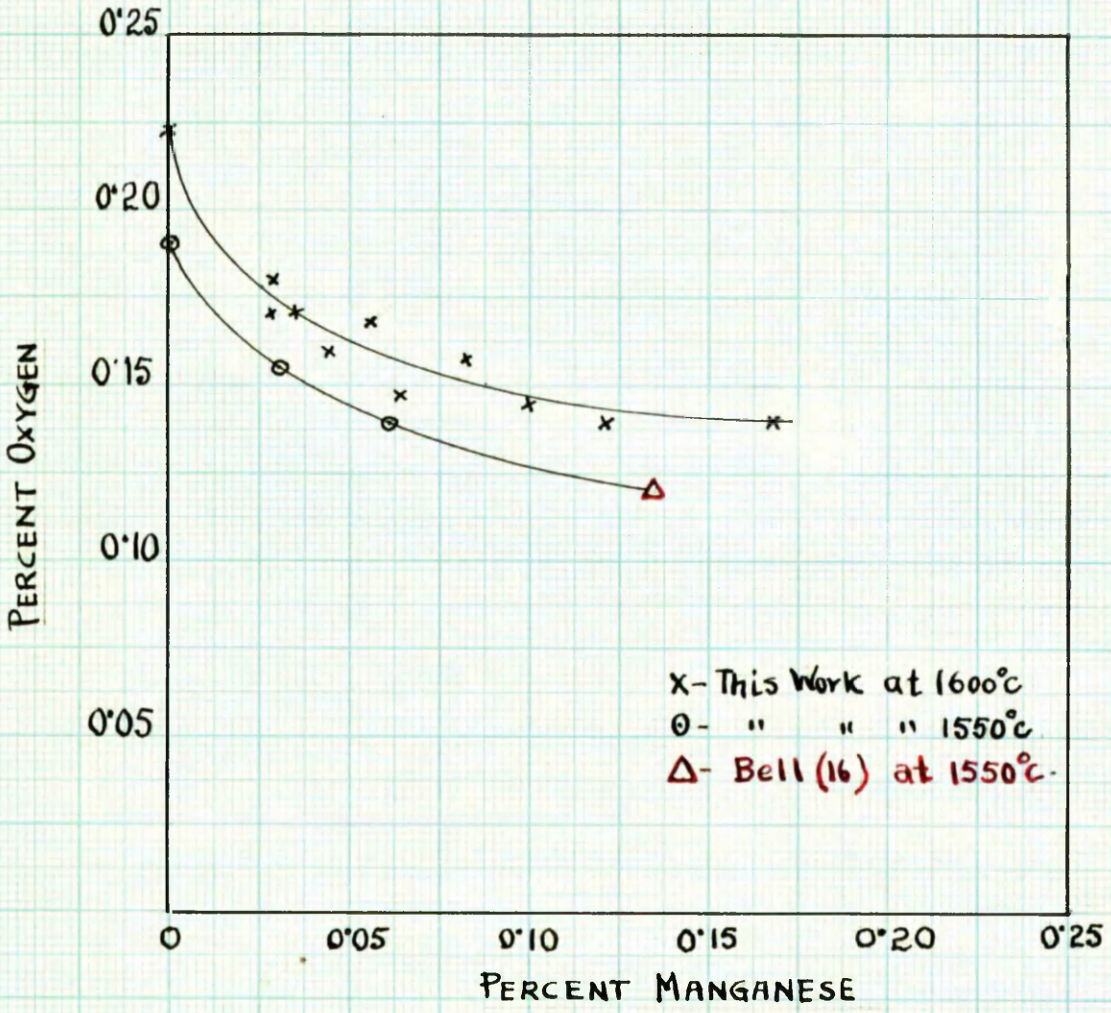


FIG 22 MANGANESE-OXYGEN EQUILIBRIUM IN LIQUID IRON IN ABSENCE OF SILICON.

CHAPTER 6.

EQUILIBRIA OF SILICA SATURATED FeO-MnO-SiO_2 SLAGS WITH MOLTEN IRON.

EQUILIBRIA OF SILICA SATURATED FeO-MnO-SiO_2 SLAGS WITH MOLTEN IRON.

(i) K'_{Mn} under silica-saturated slags.

The results of experiments, carried out in SiO_2 crucibles at 1550°C and 1600°C, are shown in Table 8. Values of K'_{Mn} obtained from the equation:

$$K'_{Mn} = \frac{(MnO)}{(\Sigma FeO)[\%Mn]}$$

are also shown in Table 8.

The mean values of K'_{Mn} at 1550°C and 1600°C are 15.95 and 13.3 respectively. The most extensive investigation of K'_{Mn} in silica saturated slags is that of Körber and Oelsen(37). Their experimental results showed considerable scatter (eg., from 9 to 20 approximately) but mean values of 15.5 and 11.7 at 1550°C and 1600°C respectively can be calculated from the equation given by Körber and Oelsen(37) to express the relationship between K'_{Mn} and temperature, viz.,

$$\log K'_{Mn} = \frac{7940}{T} - 3.172$$

In a method similar to that used in the present investigation, Bell(16) obtained a value of 15.5 for K'_{Mn} at 1550°C. The present value at 1550°C is in excellent agreement with the results of both Körber and Oelsen(37) and Bell(16) at this temperature. Recently Schenck and Wiesner(29) have also carried out determinations for K'_{Mn}. No numerical data are given but values of K'_{Mn} varying from 10-20 were obtained at 1540°C.

The value of K'_{Mn} at 1600°C obtained in the present work is rather higher than that given by Körber and Oelsen(37), whose mean

TABLE 6.

Melts Made in Silica Crucibles.

TEMPERATURE - 1600°C.

Run	Slag Analysis Weight %			Slag Analysis Mole Fraction			Metal Analysis			K'_{Mn}	$K_{Si} = \frac{[O]^2}{[Si]} \times 10^3$	a_{FeO}	γ_{FeO}	γ_{MnO}
	ΣFeO	MnO	SiO_2	ΣFeO	MnO	SiO_2	Mn	Si	O					
33	30.2	18.1	51.7	.274	.166	.55	.048	.033	.032	12.45	2.70	.275	1.00	.25
34	25.2	24.8	50.0	.229	.228	.54	.07	.013	.046	14.07	2.75	.204	.91	.21
35	23.4	26.3	50.3	.212	.242	.546	.084	.026	.038	13.33	3.7	.17	.81	.19
36	15.7	34.1	50.3	.142	.313	.545	.16	.032	.039	13.30	2.88	.133	.94	.21
37	18.0	34.5	48.4	.161	.315	.523	.145	.025	.035	13.21	3.06	.155	.96	.23
38	13.0	36.9	50.1	.118	.339	.542	.208	.034	.028	13.6	2.6	.142	1.05	.27
39	9.4	39.0	51.6	.087	.357	.558	.31	.093	.0172	13.45	2.72	.08	0.92	.22
											TEMPERATURE - 1550°C.			
49	21.3	30.3	48.6	.193	.279	.528	.09	N.D.	N.D.	15.8	N.D.	N.D.	N.D.	N.D.
50	17.3	34.1	48.6	.157	.314	.529	.128	N.D.	N.D.	15.09	N.D.	N.D.	N.D.	N.D.
51	10.4	40.3	49.2	.094	.371	.535	.242	N.D.	N.D.	16.07	N.D.	N.D.	N.D.	N.D.

value appears to lie outside the limits of experimental error of the present work. Their value would correspond to about 11.7 at 1600°C and it is again probable that at higher temperatures errors were introduced into their temperature measurements leading to low readings. It is also possible that some of their slags were not saturated with silica which again would result in low values of K'_{Mn}.

Although the temperature range of the present work is only 50°C, the scatter of the individual points at 1550°C and 1600°C is sufficiently small to justify the calculation of a relation between K'_{Mn} and the temperature, and is shown in Figure 23. This may be represented by the equation:

$$\text{Log } K'_{Mn} = \frac{5250}{T} - 1.670.$$

This leads to a value for the free energy of the equation.

$$[Mn]\ 1\% + (FeO)_{SiO_2 \text{ saturated}} = Fe(\ell) + (MnO)_{SiO_2 \text{ saturated}}$$

$$\Delta G^{\circ} = -24020 + 7.64T$$

If this is combined with the free energy change for this reaction under simple oxide slags and the assumption is made that the free energy of formation of silica saturated iron-silicate from ferrous oxide and silica is very small, a value of -5320 calories can be deduced for the free energy of formation of silica saturated manganese-silicate from manganous oxide (liquid) and silica at 1600°C. As this composition is very close to that of rhodonite this may be taken as a first approximation as the free energy of formation of rhodonite from manganese oxide (liquid)

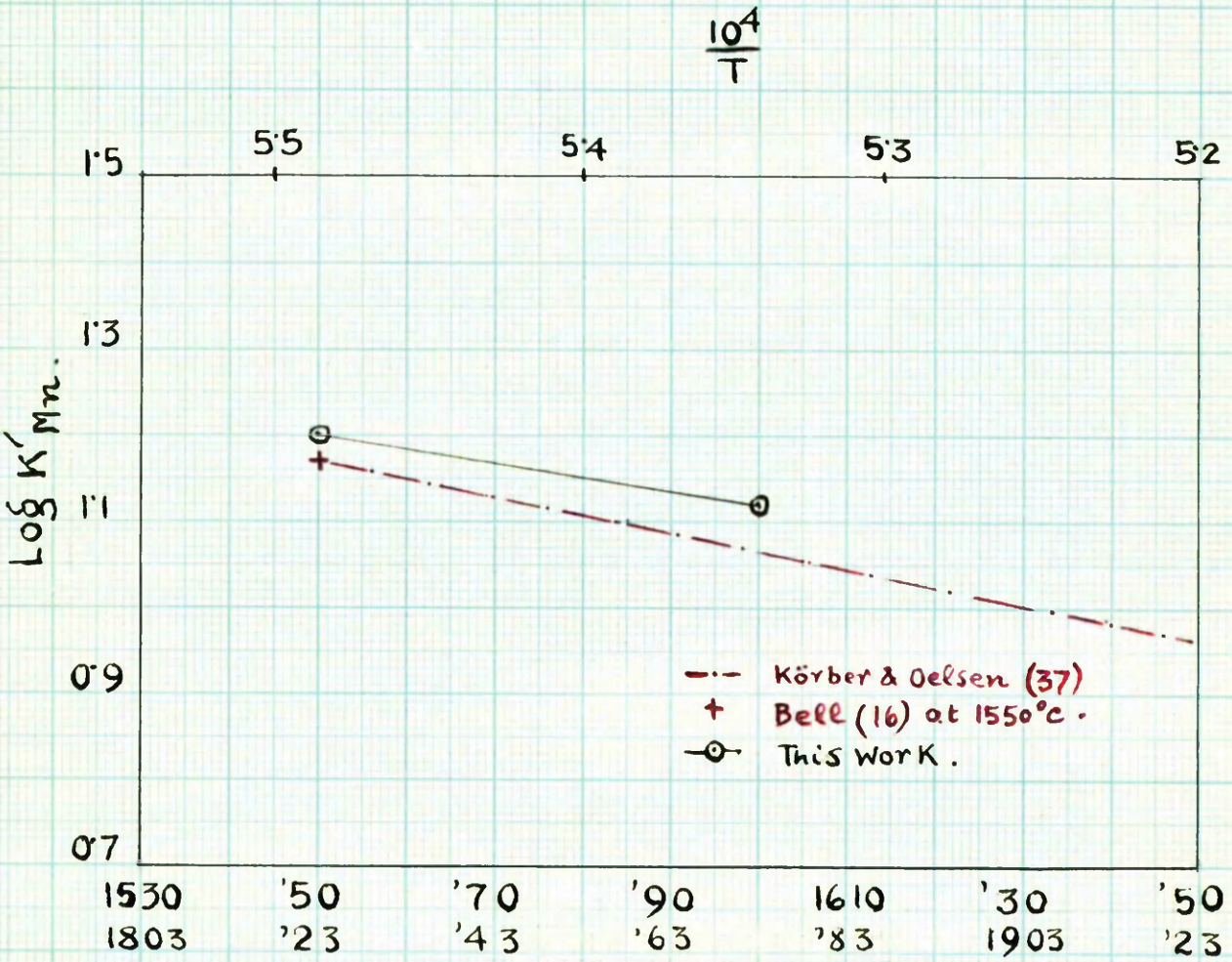
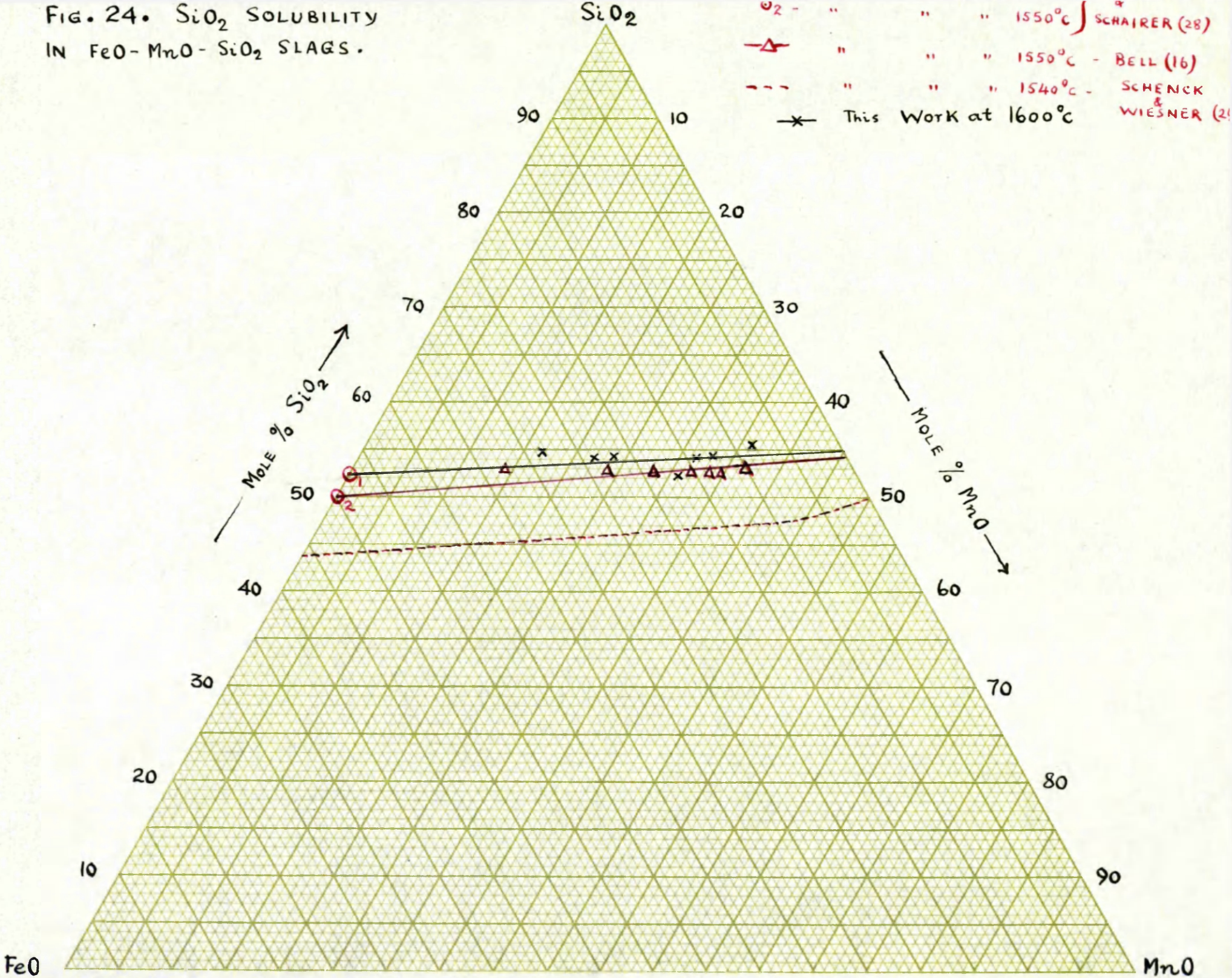


FIG.23. VARIATION OF Log K'_{Mn} WITH TEMPERATURE IN SILICA SATURATED FeO - MnO - SiO_2 SLAGS.

and silica. A slight correction will be necessary as the activity of silica will be slightly less than unity. Rey(52) has calculated a value of about 0.8 from the $MnO-SiO_2$ phase diagram and allowing for this the free energy of formation of rhodonite becomes approximately - 6000 cals. Richardson, Jeffes and Withers(3) have calculated a value of -10,000 calories from earlier results on the manganese reaction but pointed out that this value was approximately 5000 cals. more negative than that which might reasonably be expected from the results of calorimetric determinations of the free energy of formation of solid rhodonite from the solid oxides when appropriate allowance is made for the effects of changes of state.

Recent work of Schenck and Wiesner(29) on silica saturated $FeO-MnO-SiO_2$ system brings out a different silica solubility value than what has been given by Bowen and Schairer(28). Figure 4 shows the part of the $FeO-SiO_2$ diagram given by Bowen and Schairer(28) along with the new solubility line given by Schenck and Wiesner(29). From their publication, unfortunately, no actual analytical data are available but Figure 4 of their article shows as much as 7 percent scatter in their silica solubility values. The present investigation at 1550°C and 1600°C is in better agreement with that of Bowen and Schairer(28). Silica solubility value obtained in the present work at 1550°C also confirms the findings of Bell(16). As regards $MnO-SiO_2$ side of the diagram, Schenck and Wiesner's (29) data when compared with Murad's(48) suggests that the former's silica analyses are low. All these data are summarised in Figure 24.

FIG. 24. SiO_2 SOLUBILITY IN FeO - MnO - SiO_2 SLAGS.



(11) Activity of FeO in Silica saturated FeO-MnO-SiO_2 Slags.

Assuming that the silicon concentration met with in experiments with silica saturated FeO-MnO-SiO_2 slags does not affect f_O, then :

$$[a_O] = [\%O]$$

The activity of FeO may then be calculated from.

$$a_{FeO} = \frac{[\%O]}{\text{Saturation } [O]}$$

values of a_{FeO} calculated in this manner from results obtained at 1600°C are shown in Table No.8. Values of $\gamma_{FeO} = \frac{a_{FeO}}{N_{FeO}}$ have also been calculated and indicate a slight negative deviation from ideality. The activity of FeO in silica saturated FeO-SiO_2 slags has been determined by Golcen and Chipman(31) at 1600°C, Fischer and Vom Ende(14) at 1500°C, and Schuhmann and Ensio(30) at the melting point of iron, the values obtained being 0.39, 0.43 and 0.377 respectively. These correspond to γ_{FeO} = 0.83, 0.90 and 0.81 respectively. The mean value for γ_{FeO} of 0.94 obtained in the present work for slags which also contain MnO are slightly higher than all the above values. Bell(16) using a similar experimental procedure to that of the present work obtained γ_{FeO} = 0.87 at 1550°C for silica saturated FeO-MnO-SiO_2 slags. Although the above variations in γ_{FeO} are within the limit of experimental error, it should be pointed out that the silicon content of the metal was slightly higher in the present work than the work with FeO-SiO_2 slags and the assumption that silicon does not affect the activity of oxygen may not be completely justified. This will be referred to in detail later. The results

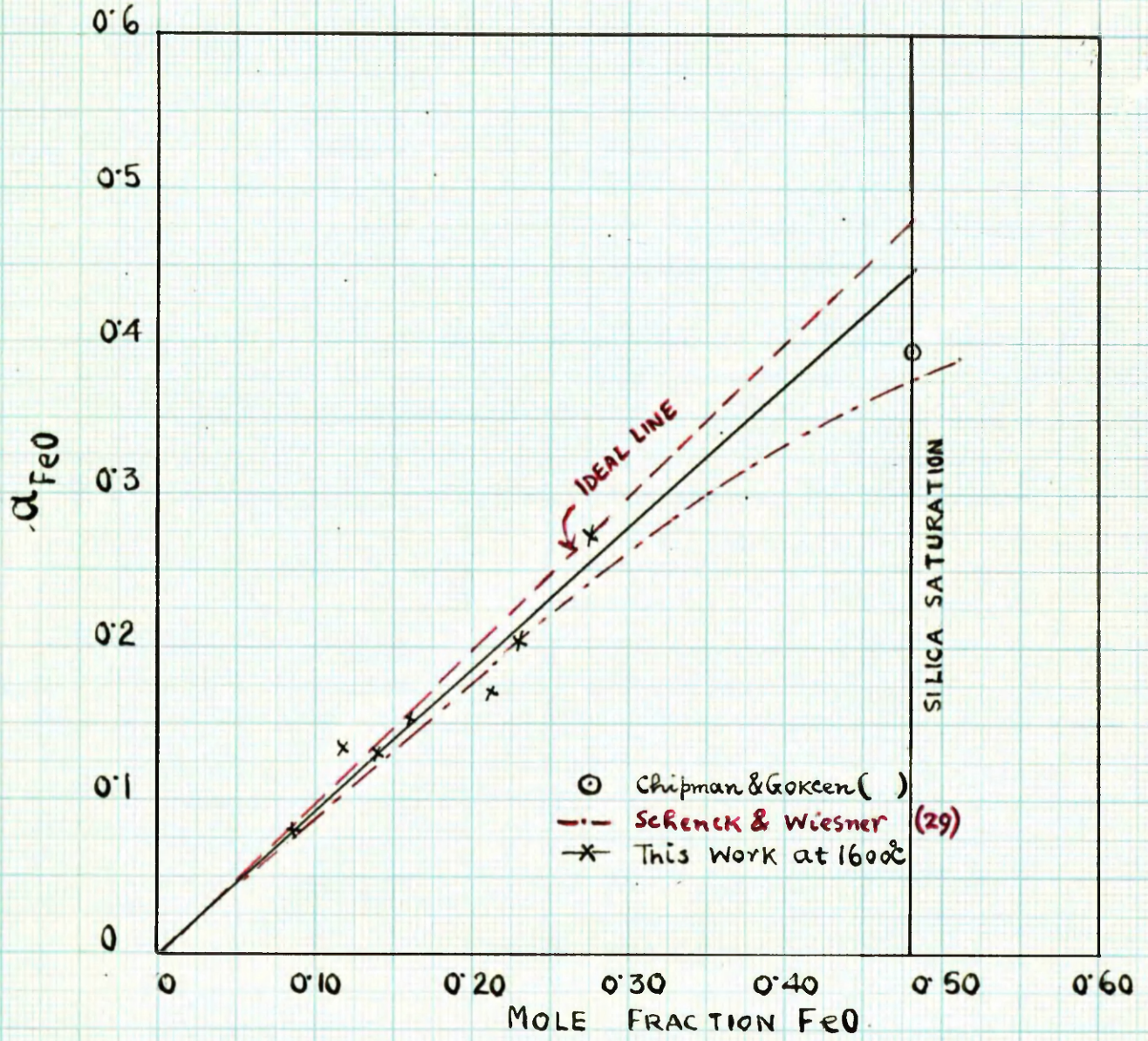


FIG. 25. ACTIVITY OF FeO IN SILICA SATURATED FeO-MnO-SiO_2 SLAGS.

indicate that MnO has little effect on γ_{FeO} in silica saturated FeO-MnO-SiO_2 slags.

The present findings are illustrated in Figure 25, from which a value of $a_{FeO} = 0.45$ may be derived for the silica saturated FeO-SiO_2 slag at 1600°C. Recent work by Schenck and Wiesner(29) has also yielded values of a_{FeO} in silica saturated FeO-MnO-SiO_2 slags at 1540°C. When a_{FeO} was plotted against N_{FeO}, the experimental points indicated a non-linear relationship, as is shown in Figure 25. The present results as also those of Bell(16) at 1550°C agree well with the initial part of the curve of Schenck and Wiesner(29). Whereas the part of their curve beyond about $N_{FeO} = 0.35$ cannot be confirmed or rejected by the present results, the shape of the curve appears surprising and again suggests that their saturation limit for silica is somewhat erroneous.

(iii) Activity of MnO in silica saturated FeO-MnO-SiO_2 Slags.

If manganese behaves ideally in Fe-Mn alloys containing small amounts of silicon and oxygen, the manganese reaction constant is given by:

$$K_{Mn} = \frac{(a_{MnO})}{(a_{FeO})[\%Mn]}$$

Hence, $a_{MnO} = K_{Mn}\,(a_{FeO})[\%Mn]$. The value of K_{Mn}, obtained from experiments with pure oxide slags at 1600°C is 3.2. Values of a_{MnO} have been calculated using this figure for K_{Mn} and the values of a_{FeO} obtained in the previous section and are shown in Table 8, along with the corresponding activity coefficients. These are considerably less than those of FeO and confirm the greater stability of manganese silicates, in

agreement with the relative cation-oxygen bond strengths of Fe^{++} and Mn^{++}. The mean value of γ_{MnO} is 0.23 which may be compared with 0.20 obtained by Bell(16) at 1550°C. If the solubility of oxygen in molten iron at 1600°C is taken as 0.225 percent instead of the higher value actually obtained by Körber and Oelsen(9), values for γ_{MnO} of 0.22 and 0.26 at 1600°C and 1650°C respectively can be calculated from the results of the latter. This value for 1600°C is in good agreement with that obtained in the present work. The combined results indicate that γ_{MnO} increases with rising temperature as might be expected since solutions usually tend towards ideality as the temperature rises.

(iv) Silicon Equilibrium under silica saturated FeO-MnO-SiO_2 Slags.

The equilibrium constant for the reaction

$$(SiO_2)_{crist.} \rightleftharpoons \underline{Si} + 2\underline{O}$$

is given by

$$K_{\underline{Si}} = \frac{[^{o}\!/\!_{o}Si]\cdot[^{o}\!/\!_{o}O]^2}{(^{o}\!/\!_{o}SiO_2)}$$

In experiments in silica crucibles the activity of SiO_2 may be taken as unity. It is more convenient to express the relationship in terms of weight percentages rather than activities. The above expression then becomes:

$$K'_{\underline{Si}} = [\%Si]\cdot[\%O]^2$$

$K'_{\underline{Si}}$ will only remain constant if the activities of silicon and oxygen equal their weight percentages, a condition for which would be that silicon

and oxygen had no mutual interaction, or if the mutual effects of silicon and oxygen on each other are such as to compensate and produce an apparent constancy over the range of compositions investigated. The true equilibrium constant is of course given by:

$$K_{Si} = f_{Si} \cdot [\%Si] \cdot f_O^2 \cdot [\%O]^2$$

The values of K'_{Si} obtained in the present work are shown in Table 8. The agreement between the individual values is fairly good except in the case of No.35. As the oxygen determination for this melt does not give high values for a_{FeO} and γ_{FeO}, it would appear that the silicon value obtained may be high. K'_{Si} values obtained in the present work are compared with those of other workers in Table 9. In preparing the table K'_{Si} values obtained by the other workers at 1550°C and 1650°C have also been included. The values obtained by Schenck(33) and Schenck and Brüggemann(36) at 1600°C are appreciably lower and must be attributed to the limitations in the experimental techniques available at that time. The results of Körber and Oelsen(37) compare well with other workers at 1550°C but becomes progressively higher at 1600°C and 1650°C, possibly because of faulty temperature readings at higher temperatures. In spite of a thermodynamically unsound interpretation of the Si-O relationship at low silicon concentration, the value obtained by Hilty and Crafts(23) for K'_{Si} at 1600°C is in excellent agreement with those obtained in the present work by Golcen and Chipman(31).

TABLE 9.

Comparison of K'_{Si} Values.

$K_{Si} \times 10^5$

Temp.	Schenck (53)	Schenck and Bruggemann (36)	Korber and Oelsen (37)	Hilty and Crafts (23)	Colcen and Chipman (31)	Bell (16)	Schenck and Wiesner (29)	This Work.
1550°C	-	-	1.34	1.6	1.05	1.35	2.0	-
1600°C	1.24	1.76	3.6	3.0	2.8	-	3.8	2.9
1650°C	-	-	10.6	5.3	7	-	7.3	-

Schenck and Wiesner[29] gave values for K'_{Si} which are appreciably higher than those of other workers at 1550°C and also much higher than those obtained by Hilty and Crafts(23), Gokcen and Chipman(31) and in the present work at 1600°C. The value at 1650°C appears to agree well with that of Gokcen and Chipman at 1650°C although it is slightly higher than the corresponding value obtained by Hilty and Crafts(23). However, Schenck and Wiesner(29) reported a fall in K'_{Si} with increase in MnO content of the slag as shown in Figure 10. Although Körber and Oelsen(37) used a mean value of their results which showed considerable scatter, Schenck and Wiesner claimed that the results of the former workers were in support of this variation of K'_{Si} with percent MnO as can be seen from a comparison of Schenck and Wiesner's mean line with the experimental points of Körber and Oelsen(37) shown in Figure 10,(lower figure). It should be noted that at high MnO contents the values obtained by Körber and Oelsen show a significant increase, which was not observed by Schenck and Wiesner(29). An even greater lowering of K'_{Si} with MnO content was observed by Schenck and Wiesner, when about 20% Al_2O_3 was added to the slags, as shown in Figure 10. The effect of CaO additions was less marked. Schenck and Wiesner were unable to give any conclusive explanation of the variation in K'_{Si} but suggested it may be due to either the use of concentrations of silicon and oxygen instead of activities, the possibility of equilibrium being with a high melting point silicate rather than with solid silica, changes occurring in the steel after sampling or an analytical error related to the varying solubility of SiO_2 particles of different sizes

in H_2SO_4, the solvent used in breaking down the samples. Their findings will be discussed later in connection with the results obtained in the present investigation. As can be seen from Figure 26 which shows the relationship between the silicon and oxygen content of iron in equilibrium with solid silica at 1600°C, manganese contents up to 0.31 percent (corresponding to MnO contents of the slag up to 39 percent) do not appear to affect this equilibrium.

It should be pointed out that deviations from the mean value of K'_{Si} due to analytical errors may be expected to be appreciable. Thus an error in the silicon determination of $\pm 0.002\%$ and in the oxygen determination of $\pm 0.002\%$ would combine to give a value of K'_{Si} varying from 2.5 to 3.2 due to the very low concentrations of silicon and oxygen which were met in the study of this equilibrium.

The relationship between the manganese and silicon contents of molten iron in equilibrium with solid silica at 1600°C is shown in Figure 27. Although the range of concentrations of manganese and silicon is narrow and the number of points is small, it appears of value to compare these results with those of other workers on the manganese-silicon relationship. The points conform reasonably well with the mean line of Körber and Oelsen(37) for 1600°C but deviate considerably from that of Hilty and Crafts(23), especially at low silicon concentration. The results of Bell(16) at 1550°C also confirm the work of Körber and Oelsen(37) rather than that of Hilty and Crafts(23).

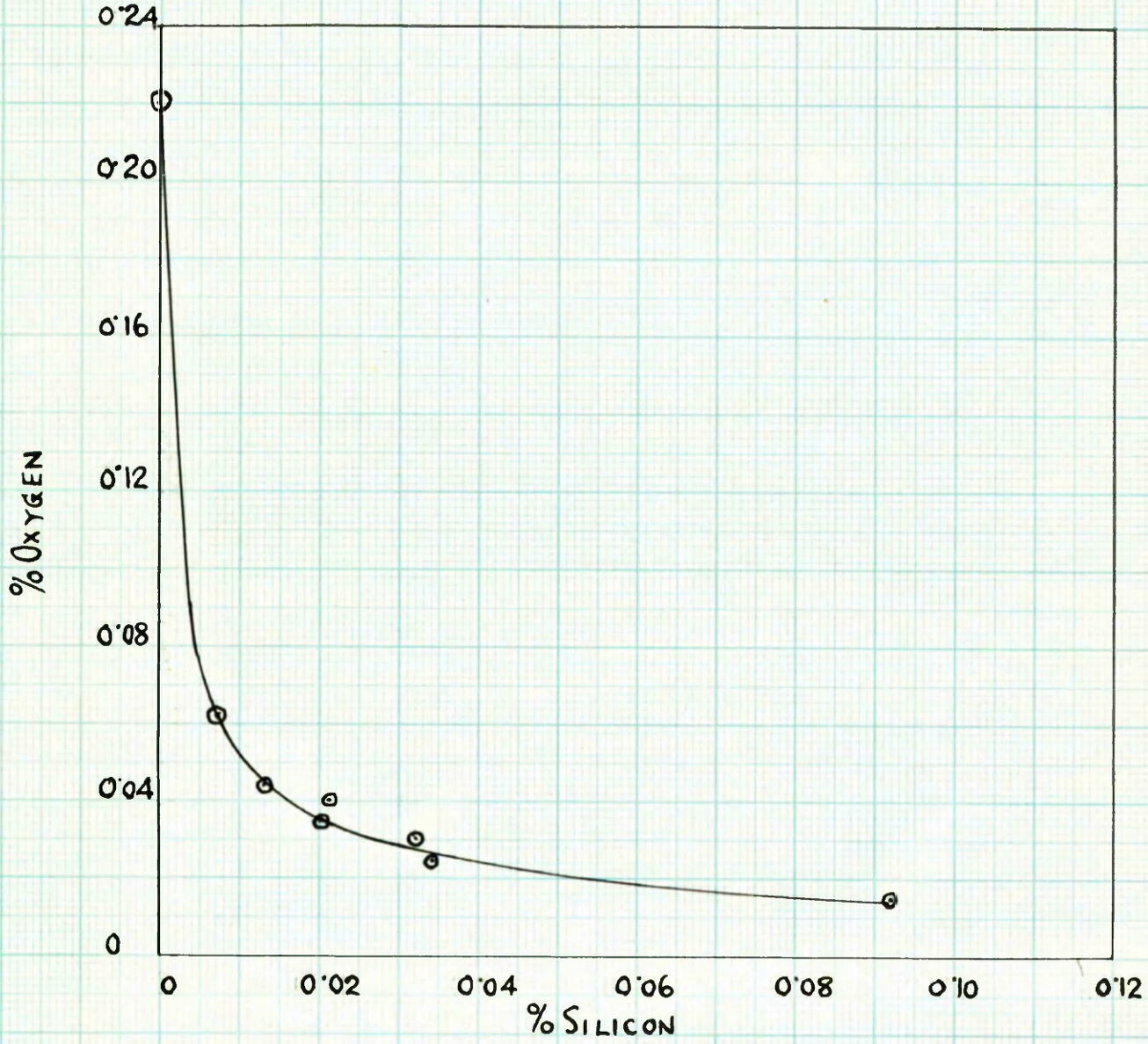


FIG. 26. Si - O EQUILIBRIUM IN MOLTEN IRON AT 1600°C UNDER SILICA SATURATED FeO - MnO - SiO_2 SLAGS.

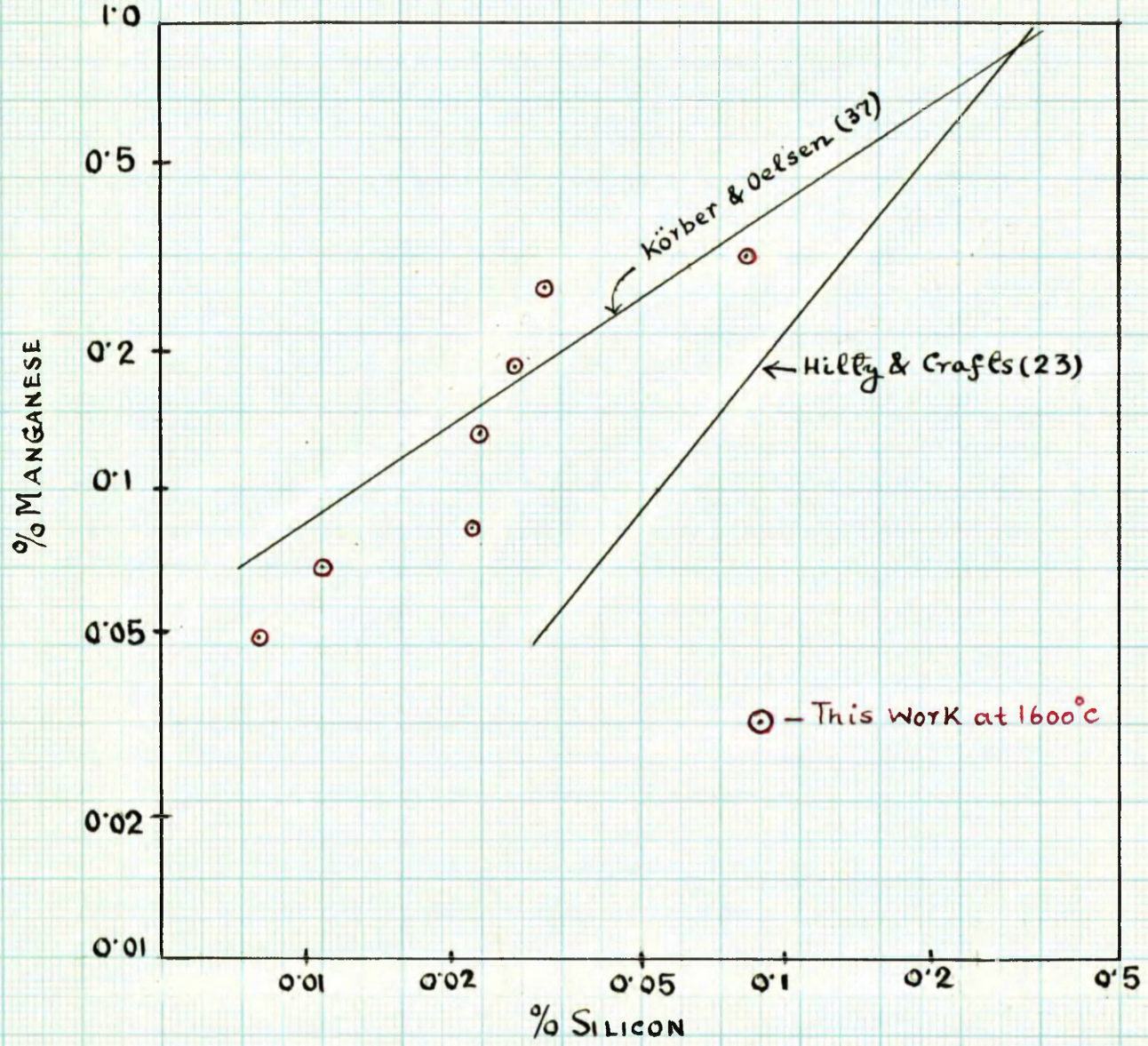


FIG.27. Mn – Si EQUILIBRIUM IN MOLTEN IRON AT 1600°C UNDER SILICA SATURATED FeO-MnO-SiO_2 SLAGS.

CHAPTER 7.

EQUILIBRIA OF SLAGS NOT SATURATED WITH SILICA WITH MOLTEN IRON.

EQUILIBRIA OF SLAGS NOT SATURATED WITH SILICA WITH MOLTEN IRON.

(1) Oxygen Equilibrium.

Results obtained on silica-free and silica-saturated FeO-MnO slags in equilibrium with molten iron represent two extremes in the study of experiments with FeO-MnO-SiO_2 slags. Wide variations in K'_{Mn} and activity values occur between these two extremes and it was proposed to make gradual silica additions to FeO-MnO slags up to silica saturation to find how K'_{Mn} and the activities of FeO and MnO varied with silica content. The results of melts carried out for this purpose are presented in Table 10. Although it would have been desirable to carry out experiments up to silica saturation in the melt, the pick up of magnesia, from the crucibles used, rose progressively with increasing silica additions, consequently silica additions were restricted to 0.32 moles. Higher additions of silica would have led to magnesia contents so high as to make interpretation of the results obtained difficult or uncertain. Even in the experiments which were actually carried out, appreciable amounts of magnesia were picked up and the system can no longer be treated as a simple ternary. To maintain conformity with previous workers and also for convenience MnO and MgO have been taken together as basic oxides and slag compositions plotted as belonging to the pseudo-ternary system FeO-(MnO,MgO)-SiO_2.

TABLE 10.

TEMPERATURE - 1600°C.

Run	Metal Analysis %			Slag Analysis Weight %						Slag Mole Fraction.				K'_{Mn}	a_{FeO}	γ_{FeO}
	Mn	O	Si	FeO	Fe_2O_3	ΣFeO	MnO	SiO_2	MgO	ΣFeO	MnO	SiO_2	MgO			
15	.093	.171	<.001	62.3	7.5	70.7	20.4	3.2	5.9	.67	.196	.036	.10	3.1	.76	1.13
16	.096	.137	.0015	54.6	7.4	62.8	25.5	4.1	7.5	.568	.242	.046	.124	4.2	.61	1.03
17	.045	.168	<.001	65.9	7.5	74.2	12.8	5.6	8.0	.686	.12	.062	.132	3.8	.75	1.09
18	.039	.152	.0015	57.4	4.2	62.1	23.2	7.1	7.7	.576	.218	.078	.127	4.2	.67	1.17
19	.09	.169	<.001	55.1	4.2	60.8	25.3	7.3	7.1	.565	.241	.09	.117	4.6	.75	1.33
20	.08	.121	.002	58.9	4.3	63.7	20.8	7.8	7.8	.594	.195	.087	.128	4.1	.54	.93
21	.099	.119	.002	46.1	3.9	50.4	31.0	11.1	9.8	.448	.279	.118	.155	6.2	.533	1.2
22	.16	.106	.002	39.7	3.2	42.6	37.9	13.3	6.0	.396	.357	.147	.10	5.55	.47	1.19
23	.113	.109	.001	38.1	3.6	42.1	29.9	15.0	13.1	.377	.267	.156	.201	6.3	.49	1.3
24	.135	.114	.0022	34.9	3.5	38.8	32.3	15.0	13.8	.338	.285	.156	.215	6.2	.506	1.5
25	.14	.106	.0022	31.7	2.6	34.6	34.8	17.8	13.0	.30	.31	.185	.201	7.2	.47	1.57
26	.083	.111	.002	33.5	2.3	36.0	24.5	20.2	18.3	.31	.211	.205	.278	8.2	.50	1.61
27	.093	.104	.003	33.3	2.5	36.0	25.7	20.4	18.0	.32	.22	.21	.26	7.7	.46	1.44
28	.220	.078	.008	24.5	1.6	25.9	39.2	22.0	12.7	.226	.347	.23	.198	6.99	.347	1.54
29	.072	.123	.0025	32.5	3.0	36.0	21.5	22.4	20.0	.30	.180	.223	.30	8.3	.546	1.82
30	.142	.058	.009	24.0	2.3	26.5	32.1	23.4	17.6	.218	.277	.238	.266	8.5	.26	1.2
31	.22	.051	.001	14.2	1.8	16.2	33.4	27.3	22.9	.131	.274	.265	.338	9.4	.227	1.73
32	.18	.046	.014	14.3	1.6	16.1	31.2	32.2	19.0	.134	.263	.321	.282	10.7	.204	1.52.

(11) Oxygen Solubility.

The oxygen contents of molten iron in equilibrium with various $FeO-(MnO,MgO)-SiO_2$ slags at 1600°C are shown in Fig.28. The oxygen contents of molten iron in equilibrium with oxide slags and silica saturated slags, discussed earlier, are also included. Oxygen solubilities for $FeO-SiO_2$ binary slags have been calculated from extrapolated FeO activities based on the work of Schuhmann and Ensio(30). Activities of FeO in these slags have been calculated by dividing the oxygen content of the metal in equilibrium with these slags by the oxygen saturation value at 1600°C. This assumes that the silicon and manganese concentrations encountered in these experiments do not affect the activity of oxygen. These a_{FeO} values have been given in Table 10, and are plotted against composition in Fig.29, which also indicates the approximate positions of FeO iso-activity lines for slags in the pseudo-ternary system $FeO-(MnO,MgO)-SiO_2$. The activity values obtained in experiments 16 and 19 (a_{FeO} = 0.75 and 0.546 respectively) appear to be in error and have been ignored in determining the positions of the iso-activity lines. Values of a_{FeO} obtained by Bell(16) at 1550°C for slags in this system are also shown in Fig.29. It will be seen that the iso-activity lines drawn fit both sets of data equally well and it would appear that temperature, at least within the somewhat narrow range of these two investigations, has no appreciable effect on the activity of FeO. Schuhmann and Ensio(30) have also found that within the range 1250°C - 1400°C, a_{FeO} did not vary with temperature in binary $FeO-SiO_2$ slags.

FIG. 28. OXYGEN CONTENT OF MOLTEN IRON AT 1600°C IN EQUILIBRIUM WITH FeO-(MnO+MgO)-SiO_2 SLAGS.

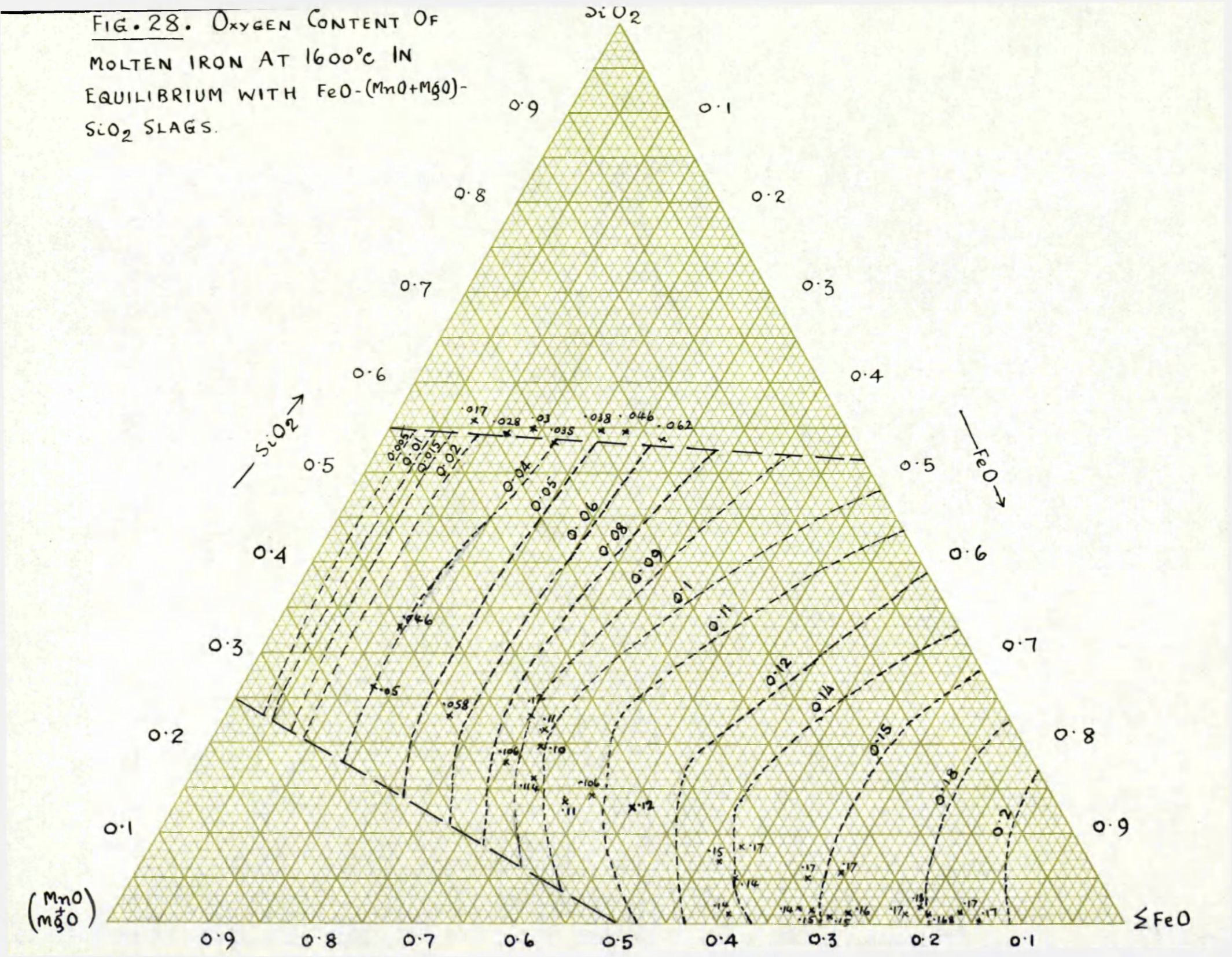
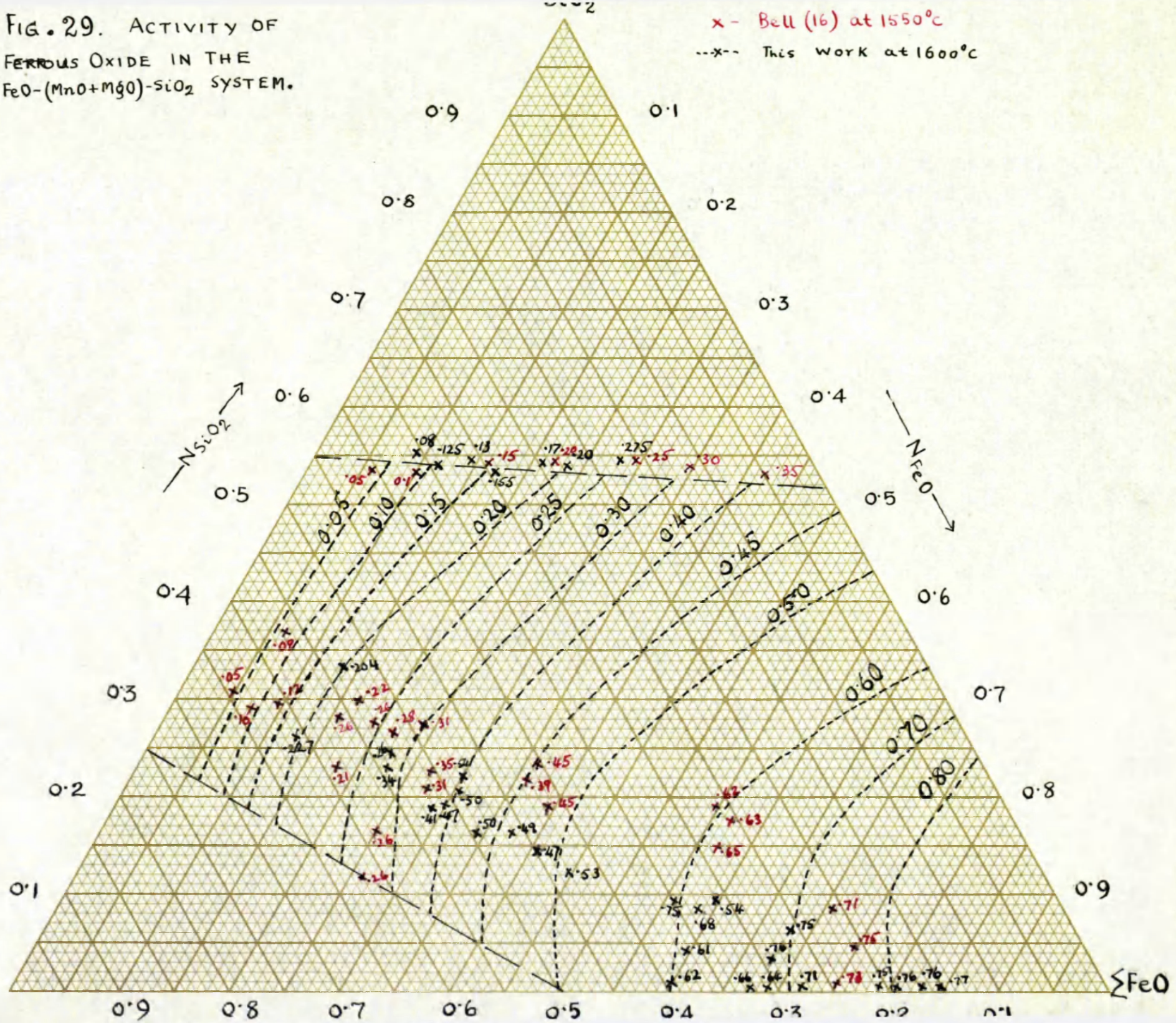


FIG. 29. ACTIVITY OF FERROUS OXIDE IN THE $FeO-(MnO+MgO)-SiO_2$ SYSTEM.



It is clear from Fig.29, that FeO does not behave ideally in $FeO-(MnO,MgO)-SiO_2$ slags but shows slight positive deviation from ideality which reaches a maximum along the $FeO-2(MnO,MgO)\cdot SiO_2$ join. An even more marked deviation along the corresponding join in the $FeO-(CaO,MgO)-SiO_2$ system was observed by Taylor and Chipman(13). It should be noted that because of the difficulty of obtaining results with slags containing more than 0.32 moles of silica, difficulty is experienced in fixing precisely the position of maximum deviation but it has been assumed that the maximum would follow the FeO-orthosilicate join in view of results obtained in similar work carried out by Taylor and Chipman(13), on $FeO-(CaO,MgO)-SiO_2$ slags shown in Fig.30.

The variation in the activity of FeO along the join $FeO.2(MnO.MgO).SiO_2$ with composition has been plotted in Fig.31. The points, which were obtained from the FeO iso-activity diagram, fall on a fairly smooth curve, which suggests that, amongst themselves the data used are not contradictory. It can be seen that the deviation from ideality along the join is not great. A similar plot is shown in the same figure of the variation of a_{FeO} against composition along the $FeO.2(CaO,MgO)SiO_2$ join calculated from the results of Taylor and Chipman(13) previously given in Fig.30. The much greater deviation from ideality in this system is immediately evident.

The positive deviation in the $FeO-CaO-P_2O_5$ system is so great as to cause separation into two liquids and the variation of a_{FeO} along the $FeO-3CaO.P_2O_5$ join due to this, and calculated from the FeO

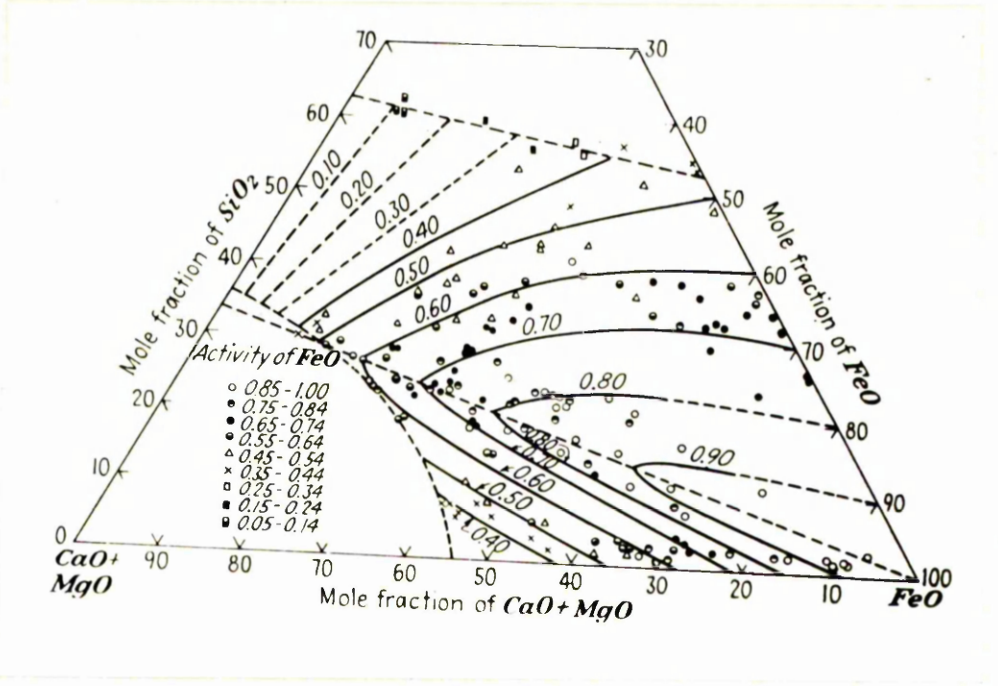


FIG. 30. ACTIVITY OF FeO IN FeO - (CaO + MgO) - SiO_2 SLAGS (TAYLOR & CHIPMAN)[13].

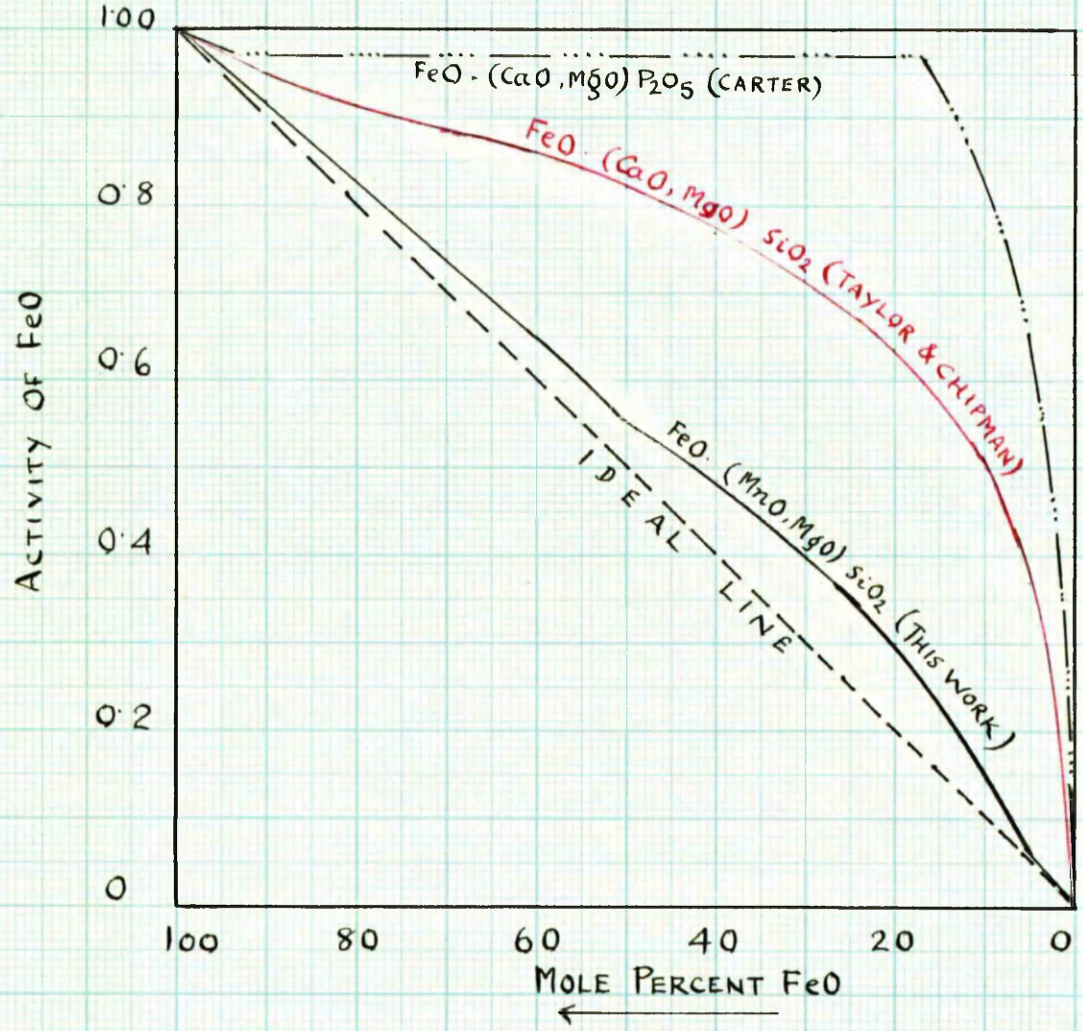


FIG. 31. ACTIVITY OF FeO ALONG $FeO - M'_2SiO_4$ OR $M'_3(PO_4)_2$ JOINS, WHERE $M' = (Ca, Mg)$ OR (Mn, Mg).

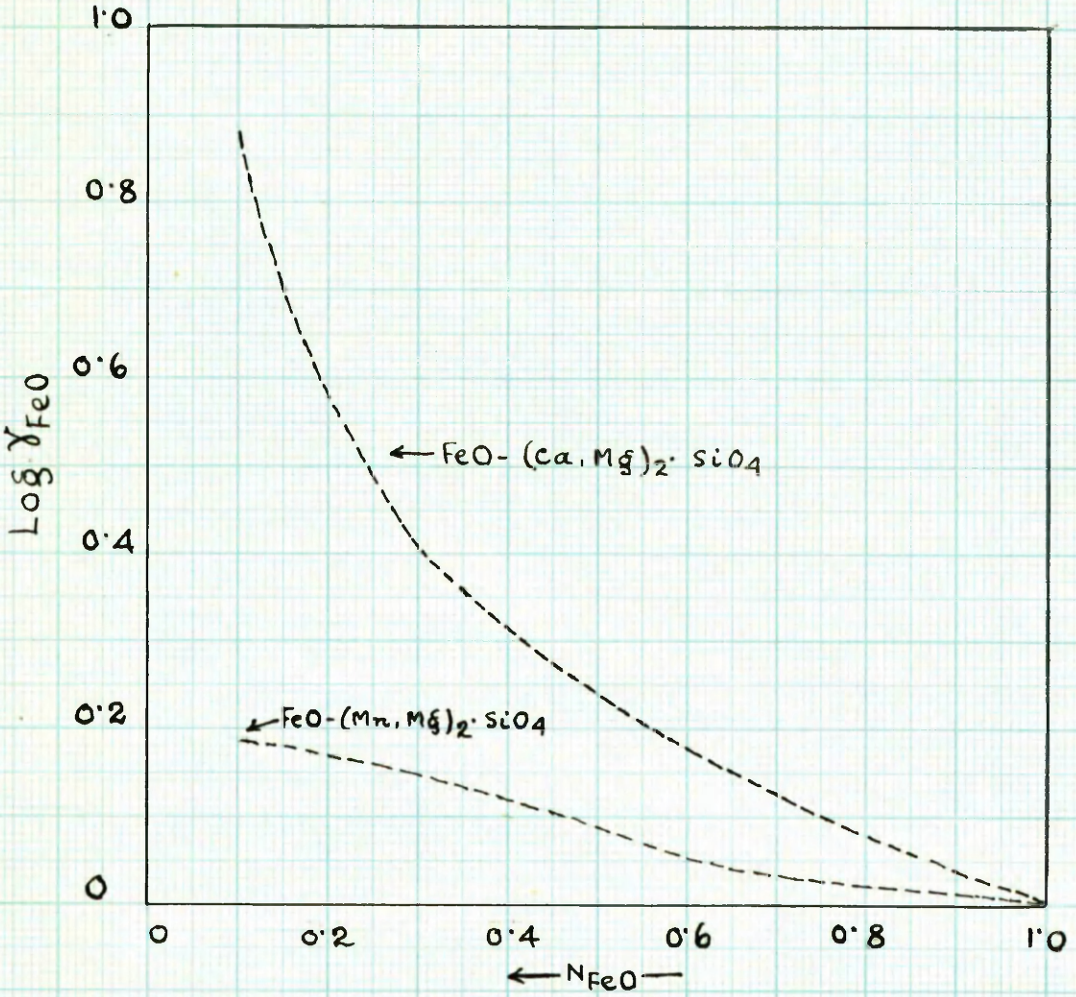


FIG. 32. VARIATION OF Log γ_{FeO} WITH FeO CONTENT ALONG FeO-$(Ca, Mg)_2 \cdot SiO_4$ AND FeO-$(Mn, Mg)_2 \cdot SiO_4$ JOINS.

iso-activity curves for this system given by Carter(54) is shown in Fig.31. The variation in γ_{FeO} along the FeO-2(MnO,MgO).SiO_2 and FeO-2(CaO,MgO)SiO_2 joins is shown in Fig.32. It has been suggested(54) that the limiting value of γ_{FeO} at $N_{FeO} = 0$ is related to the free energy change for the reaction:

$$FeO + 2MO.SiO_2 \rightleftharpoons 2FeO.SiO_2 + MO,$$

where MO is mainly MnO but containing some MgO, which is given by:

$$RT \ln \gamma_{FeO(max.)}$$

The free energy change so derived is 1.54 Kcals. This strictly refers to a mixed manganese-magnesium orthosilicate, although in the slags obtained, the metal oxide other than FeO was predominantly MnO in most cases.

(iii.) Fe_2O_3 Content of the Slag.

In preparing the iso-activity diagram for FeO shown in Fig.29, the FeO content of the slag was obtained by calculating FeO from the total iron content of the slag. As the analyses reported in Table 4 show, all the slags contained an appreciable concentration of Fe_2O_3. The amount of Fe_2O_3 decreased as the silica content of the slag increased, as can be seen from Fig.33. This trend has also been observed by Bowen and Schairer(28), Darken and Gurry(29) and Chipman and Fetters(12). For similar temperatures the Fe_2O_3 contents observed by Darken and Gurry(30) were slightly lower than those obtained by Chipman and Fetters,

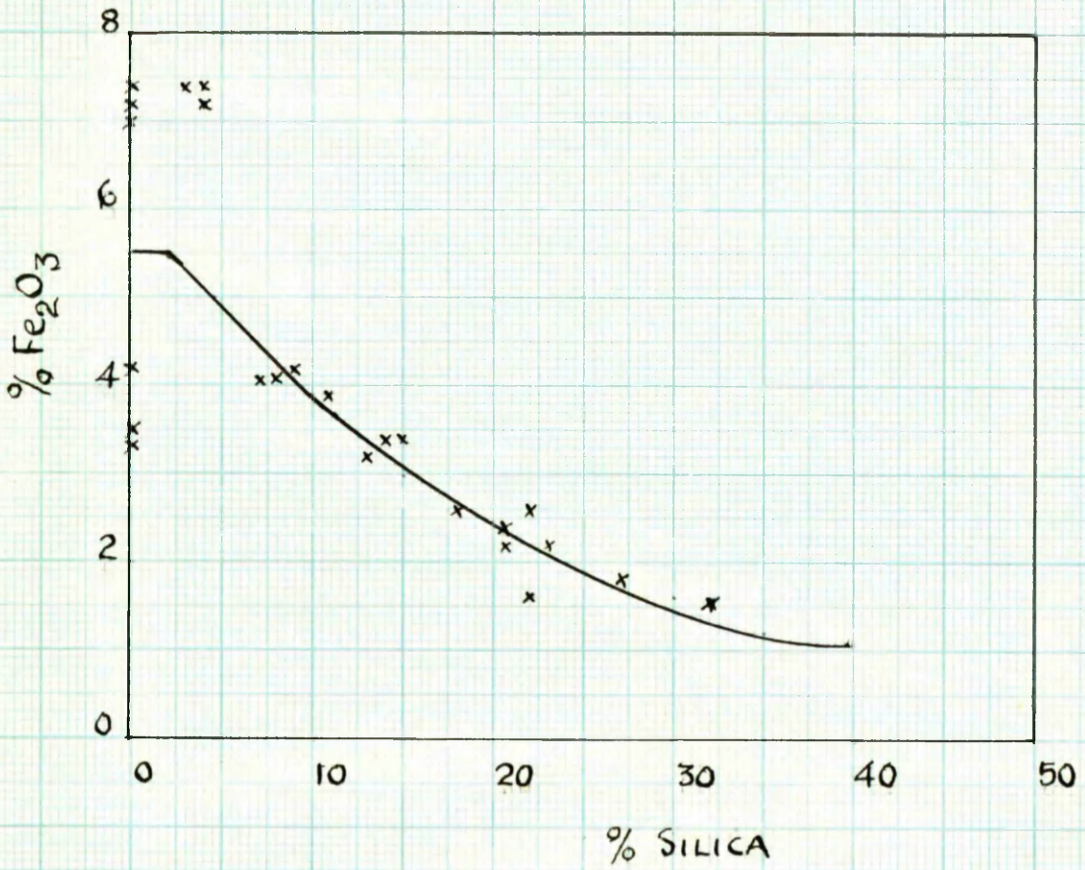


FIG.33. VARIATION OF Fe_2O_3 CONTENT WITH SILICA CONTENT OF FeO - MnO(MgO) - SiO_2 SLAGS IN EQUILIBRIUM WITH MOLTEN IRON AT 1600°C.

probably because the latter's experiments were carried out in magnesia crucibles, which raised the Fe_2O_3 content in the slag. (It is possible that MnO plays a similar role to magnesia but their individual effects cannot be separated. In support of this it may be noted that Darken and Gurry have indicated that MnO stabilises Fe_2O_3). The above activity values are therefore only valid if it is understood that the standard state for FeO is iron-oxide at the appropriate temperature and containing small percentages of Fe_2O_3.

(iv) Manganese Equilibria.

Values of K'_{Mn} obtained from all the experiments carried out have been plotted in Fig.34, as a function of the silica content of the slag. Values of K_{Mn} in the absence of silica and at silica saturation have been taken from the results of experiments carried out in magnesia crucibles (no silica additions) and silica crucibles respectively. The curve drawn indicates a gradual increase in K'_{Mn} with increasing silica content up to silica saturation. Although the results are complicated by the fact that a fourth constituent, viz., MgO has been introduced into the slag from the crucible, the increase in K'_{Mn} with silica content may reasonably be attributed to the different effects of silica on the activities of MnO and FeO. K'_{Mn} in silica saturated slags is given by,

$$K'_{Mn} = \frac{(\%MnO)}{(\%FeO)[\%Mn]} = \frac{(MnO)}{(FeO)[\%Mn]}$$

Since the molecular weights of MnO and FeO are almost identical.

$$K'_{Mn} = \frac{\frac{(a_{MnO})}{\gamma_{MnO}}}{\frac{(a_{FeO})}{\gamma_{FeO}} \cdot [\%Mn]}$$

$$= \frac{(a_{MnO})}{(a_{FeO})[\%Mn]} \cdot \frac{\gamma_{FeO}}{\gamma_{MnO}}$$

$$= K_{Mn} \cdot \frac{\gamma_{FeO}}{\gamma_{MnO}}$$

where K_{Mn} is the value obtained with pure oxide slags. At 1600°C K_{Mn} and K'_{Mn} have been found to be 3.2 and 13.3 respectively. The mean value of γ_{FeO} in silica saturated slags was found to be 0.94 . Hence, a value of 0.23 can be derived for the activity coefficient of MnO in silica saturated $FeO-MnO-SiO_2$ slags.

It is of importance to consider whether the shape and position of the curve shown in Fig.34, have been affected by the presence of magnesia in the slag. Very little experimental work has been done on the free energy of formation of manganese and magnesium silicates. A few results obtained by Flinhan and Richardson(55) indicate that magnesium silicate melts are of almost the same stability as manganese silicate melts. The addition of magnesia to $FeO-MnO-SiO_2$ melts would not therefore be expected to increase appreciably the activity of MnO. The activity of FeO in these melts is already approximately equal to its mole fraction and should remain almost unaffected. The true relationship between K'_{Mn} and the silica content of the slag in the absence of MgO might be expected to be slightly higher than the curve drawn and may not vary significantly from it within the limits of experimental

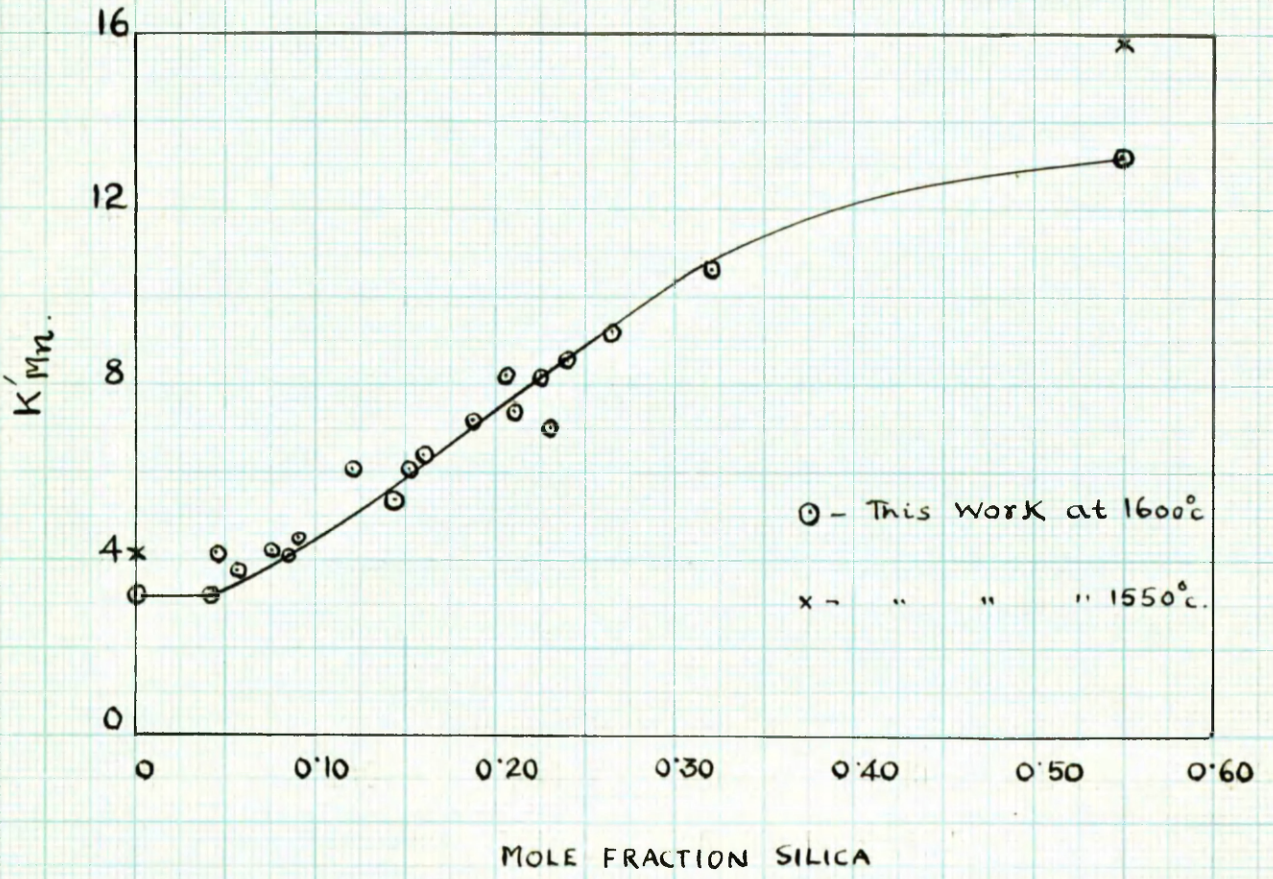


FIG.34. VARATION OF K'_{Mn} WITH MOLE FRACTION SILICA.

error. Indirect support for this conclusion may be derived from a comparison of K'_{Mn} values obtained by Krings and Schackmann(40) in experiments carried out in alumina crucibles at 1550°C with those obtained by Bell(16) in magnesia crucibles at the same temperature. The former were only very slightly lower than those obtained by Bell. As the effect, if any, of alumina additions would be expected to be the opposite of that of magnesia additions, i.e., to raise K'_{Mn}, then the K'_{Mn} curve in the absence of Al_2O_3 would be expected to be somewhat lower than that actually obtained. It would appear, therefore, that unless the results of either Krings and Schackmann(40), or Bell(16) are greatly in error, the effects of both MgO and Al_2O_3 additions are small.

If it had been assumed that FeO behaved ideally in the slags obtained in this investigation, then the variation of K'_{Mn} with silica addition could be attributed entirely to the effect of silica in lowering the activity of MnO. In this case $\gamma MnO = \frac{K_{Mn}}{K'_{Mn}}$. As γFeO is not unity a correction for this can be made by plotting $K''_{Mn} = \frac{N_{MnO}}{(a_{FeO})[\%Mn]}$ against silica content when γMnO at any given silica content is given by,

$$\gamma MnO = \frac{K_{Mn}}{K''_{Mn}}$$

This has been done in Fig.35 in which the silica concentration is expressed as mole fraction. Although there is a slight amount of scatter in the experimental points, deviation from the mean line drawn shows no obvious trend with slag composition and it may be assumed that the value of $\frac{N_{MnO}}{a_{FeO}.[\%Mn]}$ is independent of the FeO/MnO ratio for any given silica

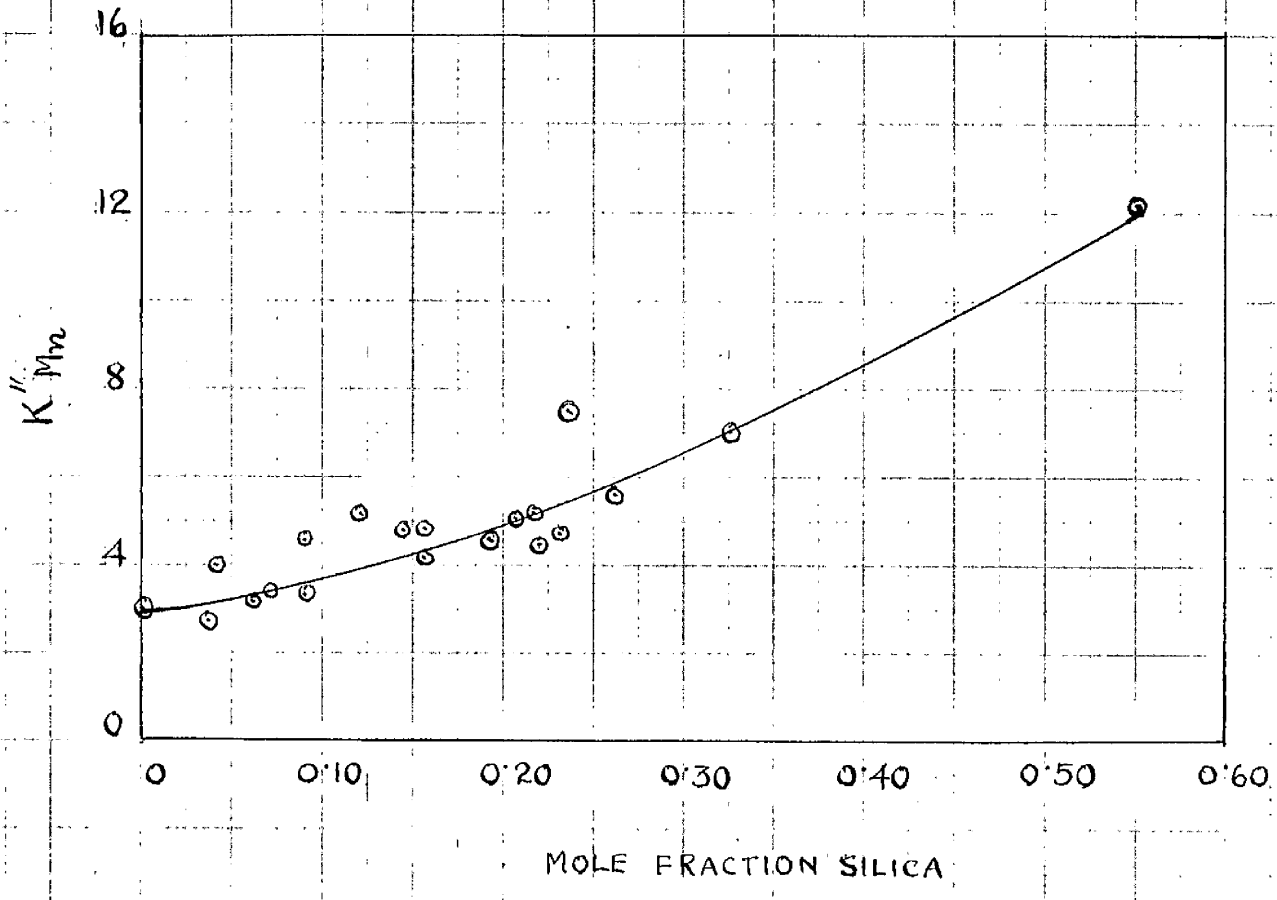


FIG. 35. GRAPH USED TO CALCULATE α_{MnO}

concentration. The activity coefficient of MnO may therefore be considered to be dependent only on the silica content of the slag at a given temperature. Assuming that magnesia acts as a diluent in FeO-(MnO,MgO)-SiO_2 slags, the values of γ MnO so obtained may be regarded as being applicable to binary MnO-SiO_2 slags. These values of γ MnO have been used to calculate ^{a}MnO in the binary MnO-SiO_2 system. Values of ^{a}MnO so obtained are plotted against N_{SiO_2} in Fig.36, and compared with those obtained by Bell(16) at 1550°C. In the range in which the slags are partly molten at 1600°C the activity values apply to super cooled liquid slags. It will be apparent that over this somewhat narrow temperature range, there is little change in the activity of MnO with temperature, although, as might be expected at higher silica contents the activities at 1600°C are slightly higher than those obtained at 1550°C indicating that as the temperature rises stability of the silicate complexes decreases.

Values of a_{MnO} for the individual slags have been calculated and are plotted against composition in Fig.37. The values of ^{a}MnO calculated above for the MnO-SiO_2 binary have also been used to assist in fixing the positions of the isoactivity lines for MnO. The presence of MgO in the slags could not be avoided and makes interpretation of the results more difficult. As an approximation MgO has been included along with FeO in constructing the diagram. If MgO and FeO are assumed to be similar in their silicate forming tendencies compared with MnO, then the isoactivity lines drawn may be regarded as applying to simple ternary FeO-MnO-SiO_2 slags.

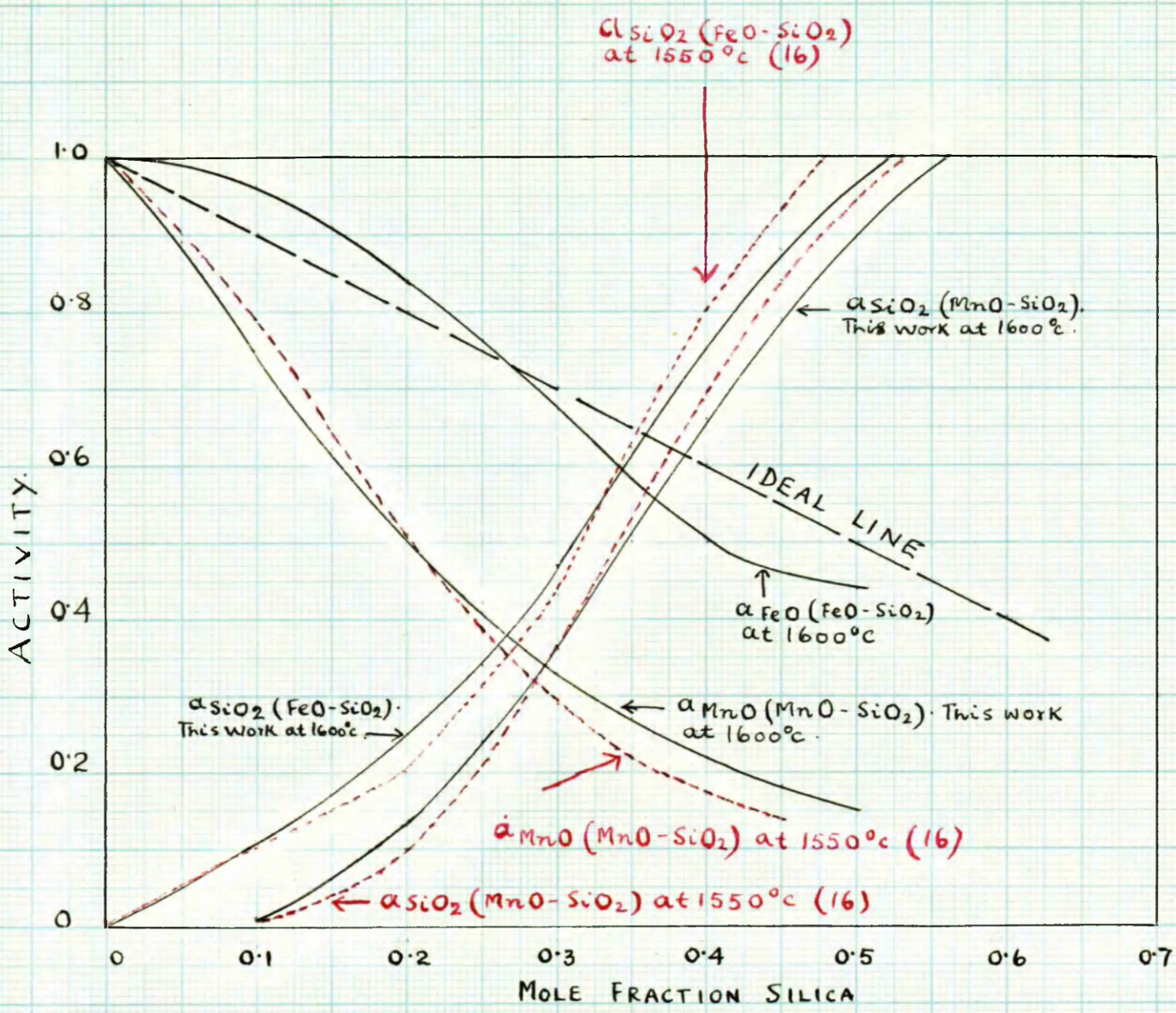
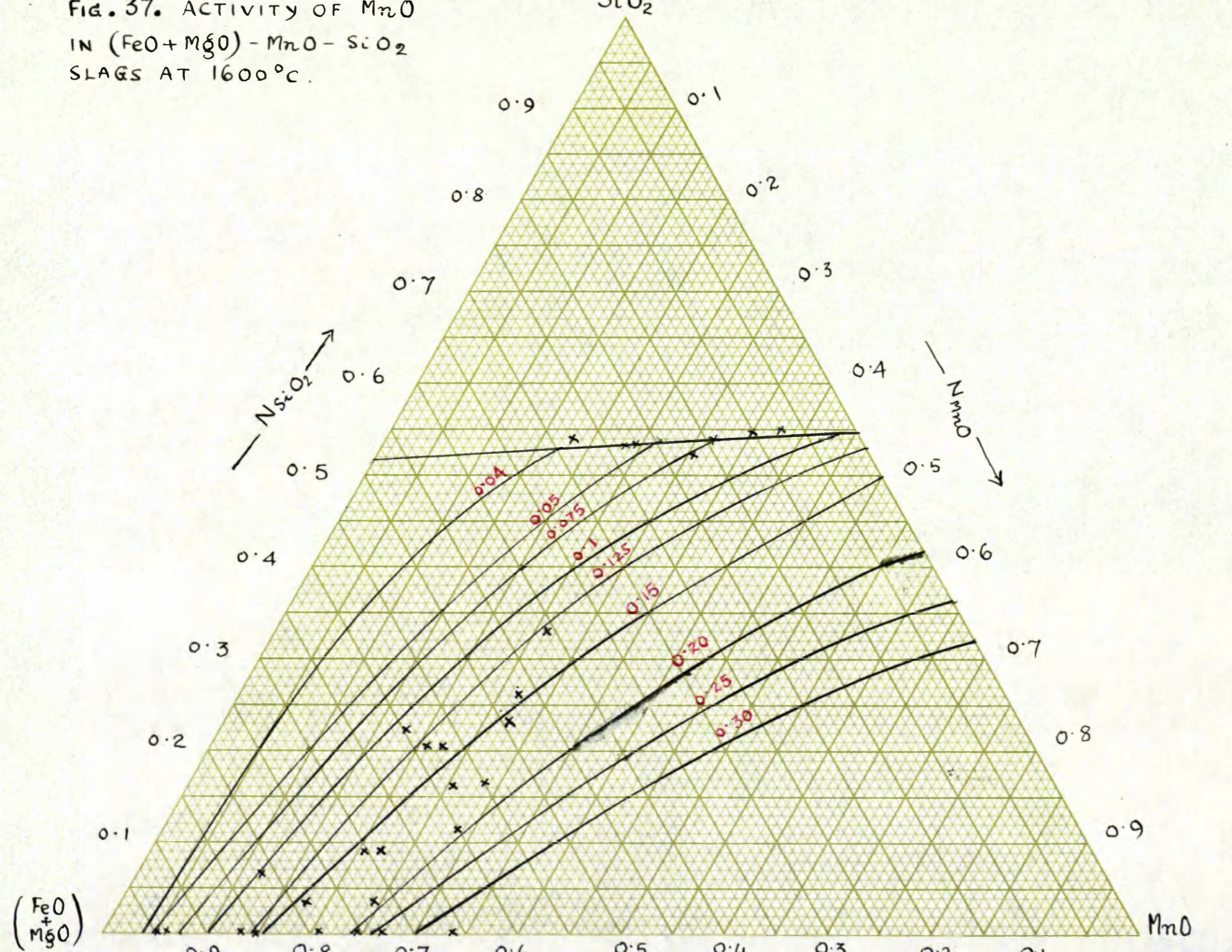


FIG. 36. ACTIVITIES IN $FeO-SiO_2$ AND $MnO-SiO_2$ SYSTEMS.

FIG. 37. ACTIVITY OF MnO IN (FeO+MgO) - MnO - SiO_2 SLAGS AT 1600°C.



Very few data are available in literature on ^{a}MnO in $FeO-MnO-SiO_2$ slags. Turkdogan and Pearson(22) have calculated values of ^{a}MnO for slags approaching silica saturation, their results being based largely on rather unreliable data obtained by Schenck(56) as long ago as 1930.

Fig.38 shows a portion of the present work (Fig.37) against the background of the MnO isoactivity curves of Turkdogan and Pearson(22). According to them these MnO isoactivity curves cannot be extrapolated beyond 0.45 mole fraction of silica without introducing errors of unknown magnitude, because the curves have inflexion points similar to those shown by FeO isoactivity curves. However, there appears to be no theoretical reason why the MnO isoactivity curves show an inflexion of the type indicated by Turkdogan and Pearson, and the results of the present work when extrapolated to the FeO-MnO binary (assuming that in the latter FeO-MnO behave ideally) indicate no such inflexion. It is, therefore, felt that the isoactivity curves obtained in the present work are more reliable than those obtained by Turkdogan and Pearson, and the discrepancy is thought to be due to the unreliable data used by Turkdogan and Pearson.

(v) Activity of Silica.

The activity of silica in binary $MnO-SiO_2$ melts, can be calculated from the values of ^{a}MnO by using the Gibbs-Duhem relationship,

$$\text{Log } \gamma SiO_2 = \int_{N_1}^{N_2} \frac{N_{MnO}}{N_{SiO_2}} \, d \log \gamma MnO$$

This has also been done for the $FeO-SiO_2$ system from the ^{a}FeO values calculated from the data of Schuhmann and Ensio(30) for 1600°C. The

FIG. 58. COMPARISON OF MnO ACTIVITIES IN FeO-MnO-SiO_2 SLAGS AT 1600°C WITH THOSE GIVEN BY TURKDOGAN & PEARSON.

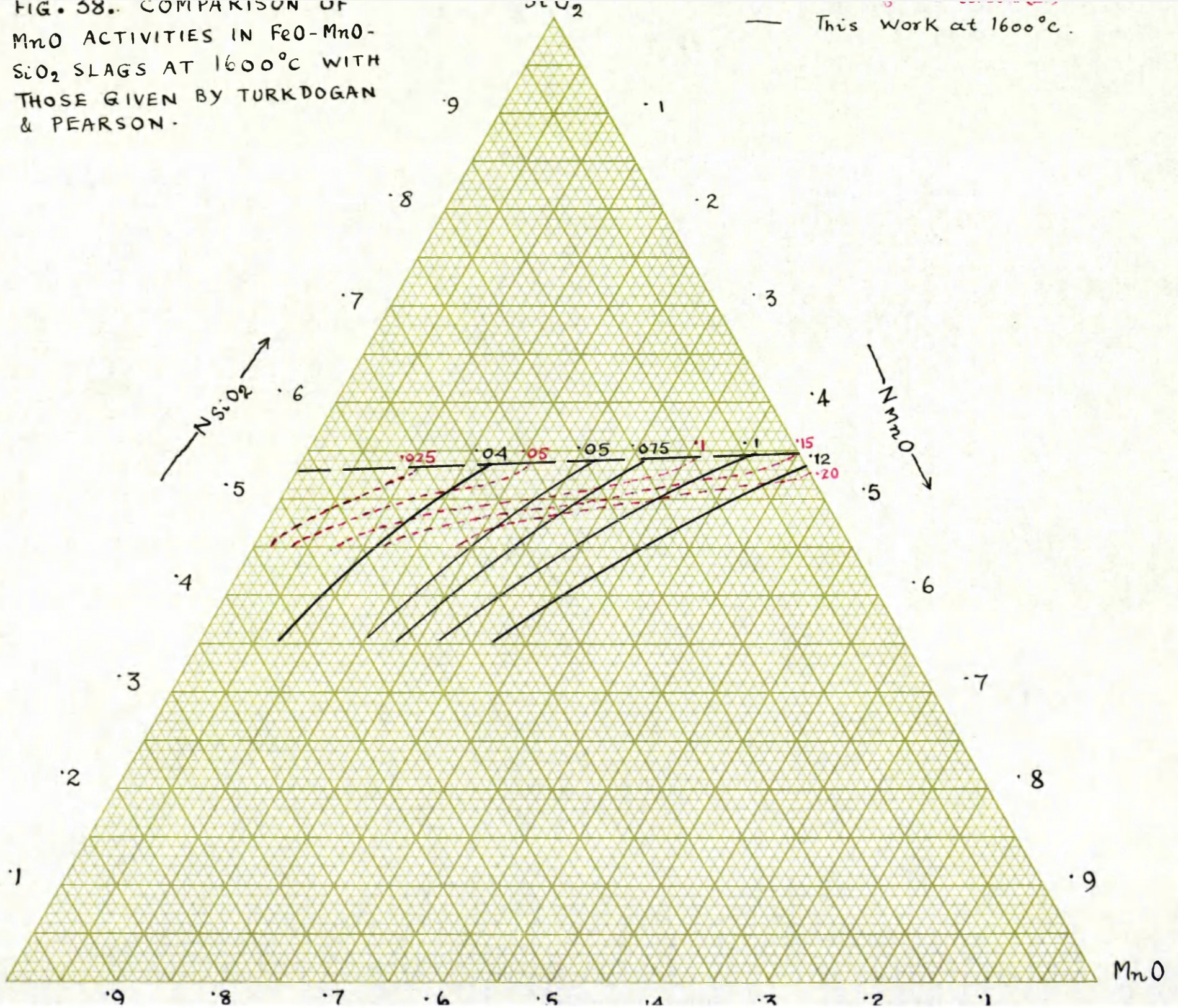
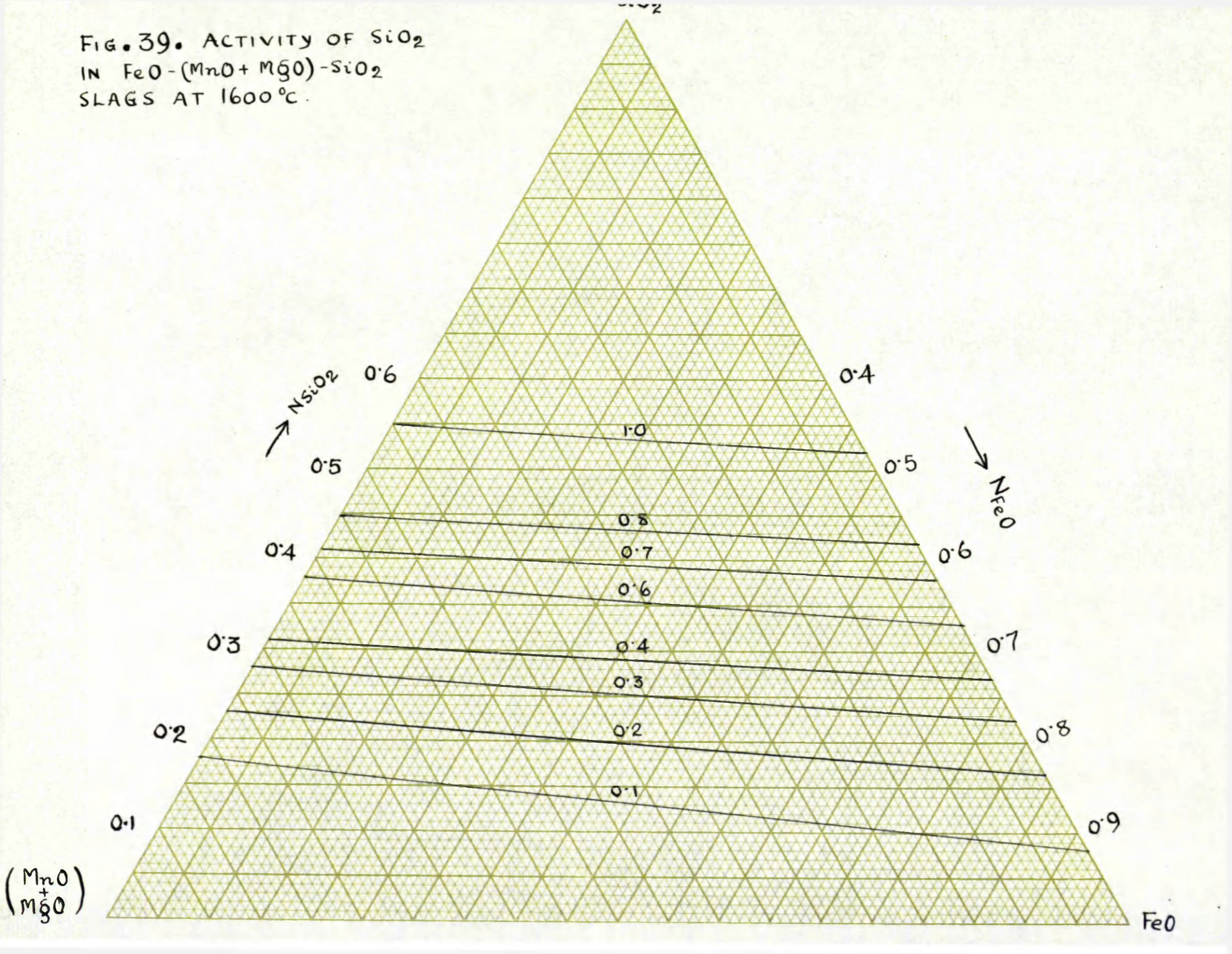


FIG. 39. ACTIVITY OF SiO_2 IN FeO - (MnO + MgO) - SiO_2 SLAGS AT 1600 °C.



values of γSiO_2 so obtained are plotted in Fig.36.

As a first approximation activities of silica in ternary melts can be obtained by linear interpolation between those for $FeO-SiO_2$ and $MnO-SiO_2$ melts. Isoactivity lines for silica obtained in this manner are shown in Fig.39.

(vi) Free energy of formation of $MnO-SiO_2$ melts.

The partial molal free energies and free energies of formation of $MnO-SiO_2$ melts at 1600°C have been calculated from the above activity data and plotted in Fig.40. The figure also shows free energies of formation curves for $FeO-SiO_2$ melts obtained from the corresponding activity data, the free energy formation of $MnO-SiO_2$ melts at 1600°C given by Richardson(57) and the curve for the free energies of formation of $CaO-SiO_2$ melts given by Carter and MacFarlane(58). The agreement with the $MnO-SiO_2$ curve of Richardson(57) obtained by a different experimental procedure is good.

As expected the curve is intermediate between those of the $FeO-SiO_2$ and $CaO-SiO_2$ systems.

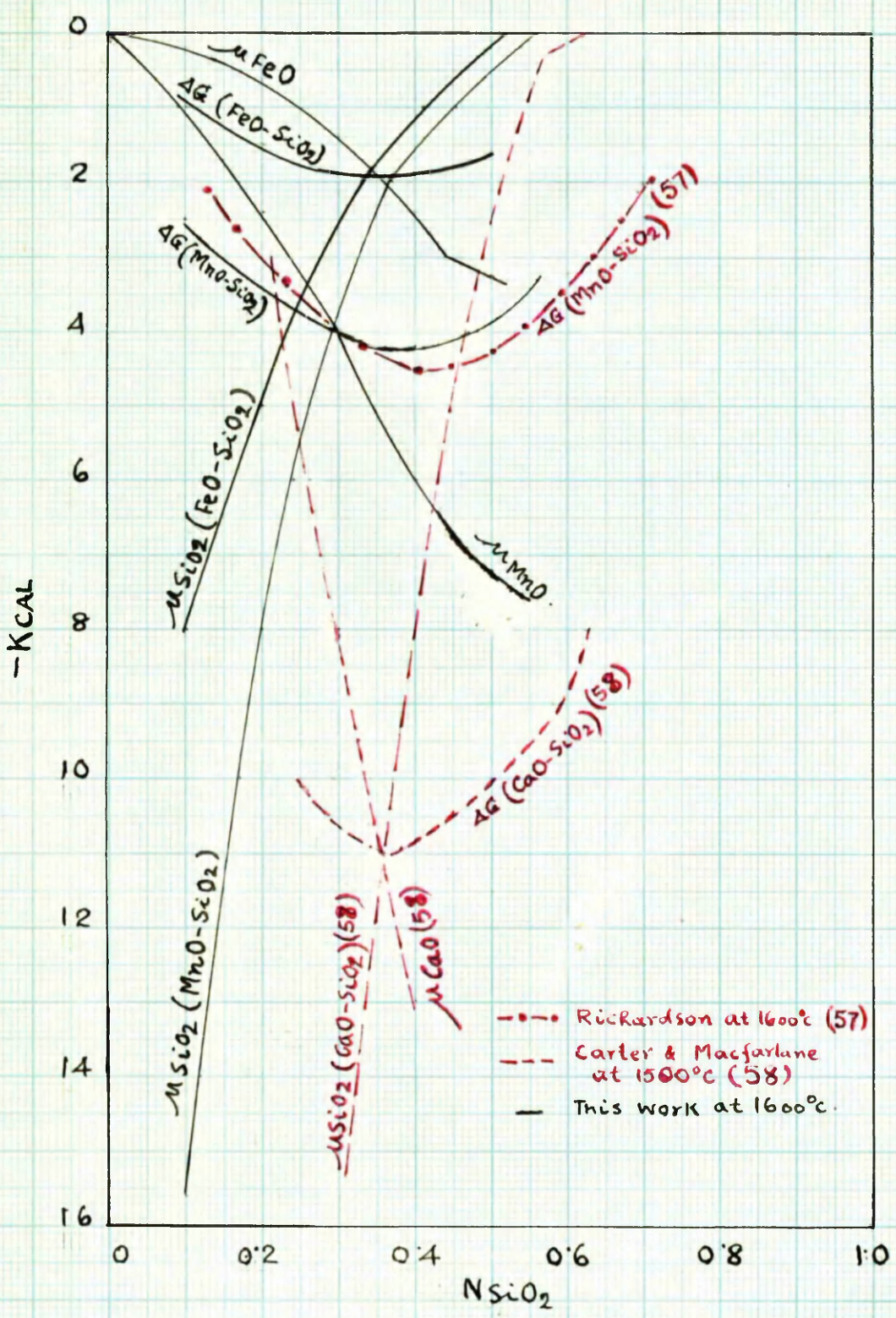


FIG. 40. FREE ENERGIES OF FORMATION AND CHEMICAL POTENTIALS OF $FeO-SiO_2$ (1600°C), $MnO-SiO_2$ (1600°C) AND $CaO-SiO_2$ (1500°C) MELTS.

(vii) Silicon equilibrium.

The silicon equilibrium may be expressed as,

$$\underline{Si} + 2\underline{O} \rightleftharpoons (SiO_2),$$

$$K_{Si} = \frac{(a_{SiO_2})}{[a_{Si}].[a_O]^2}$$

For experimental work conducted in silica crucibles and using SiO_2-saturated slags, this expression reduces to

$$K_{Si} = \frac{1}{[a_{Si}].[a_O]^2}$$

In the past it has been found more convenient to use weight percentage rather than activities when the expression

$$K'_{Si} = [\%Si].[\%O]^2$$

is obtained. K_{Si} could be regarded as a true equilibrium constant at small concentrations of silicon and oxygen, if solutions of these elements in iron obey Henry's law and if they do not affect the activity of each other. In the present work at 1600°C, K'_{Si} was found to be 2.9×10^{-3} compared with 3.0×10^{-3}, 2.8×10^{-3}, 3.6×10^{-3} and 3.8×10^{-3} obtained by Hilty and Crafts(28), Gokcen and Chipman(31), Korber and Oelsen(37) and Schenck and Wiesner(29) respectively. The agreement between the various workers can be regarded as good over the range of silicon and oxygen concentration encountered using silica saturated slags. K'_{Si} was constant within the limits of experimental error and it might appear at first sight that the activities of silicon and oxygen were equal to their weight percentages. However, the limitation of working with slags

saturated with silica does not allow exploration of a wide range of silicon and oxygen concentrations in the metal. The results obtained using magnesia crucibles and slags not saturated with silica resulted in metal samples covering a considerable concentration range, in particular, metal samples were obtained containing relatively large amounts of oxygen compared with the silicon content. It was also possible to obtain low or high silicon contents by controlling the silica concentration (and, therefore, activity) in the slag. As the silica activity is no longer unity, values of K_{Si} can only be calculated if the silica activity is known. Activities of silica in the slags were calculated by a proportional interpolation between the curves for $^{a}SiO_2$ in $FeO-SiO_2$ and $MnO-SiO_2$ slags, i.e., by assuming that the iso activity lines for silica were linear between the respective value for the binaries as shown in Fig.39. Although an error has been introduced in these interpolations for $^{a}SiO_2$ by assuming that the magnesia present has no appreciable effect on the equilibria and can be regarded as an inert diluent, it is believed that this error does not exceed 20 percent of the value obtained. These values of $^{a}SiO_2$ have been used to calculate values of $\frac{[\%Si]\cdot[\%O]^2}{(^{a}SiO_2)}$ as shown in Table 11. It will be seen that the values of this expression vary considerably.

One interpretation of this variation would be to attribute it to a mutual interaction between silicon and oxygen dissolved in molten iron. In the melts under consideration the oxygen contents are high compared with those of silicon and the main effect would be that of oxygen on the activity of silicon. Although no true value of K_{Si} is available, a close approximation may be obtained by using the mean K'_{Si} value, 2.9×10^{-3},

Slag-Metal Data for Silicon Equilibrium at 1600°C.

Run	Slag Analysis (mole fraction) ΣFeO	MnO	SiO_2	a_{SiO_2}	[%Si]	[%O]	$\frac{[\%Si]\cdot[\%O]^2}{a_{SiO_2} \times 10^{-5}}$	f^0_{Si}	$\log f^0_{Si}$
15	.67	.196	.086	.085	< .001	.171	< 80	.086	-1.44
16	.588	.242	.046	.04	.0015	.137	72.5	.04	-1.40
17	.686	.12	.062	.06	< .001	.168	< 48	.06	-1.22
18	.576	.218	.078	.08	.0015	.152	36.3	.08	-1.10
19	.565	.24	.09	.075	< .001	.169	< 39	.075	-1.13
20	.584	.195	.087	.085	.002	.121	34.1	.085	-1.07
21	.448	.279	.118	.095	.002	.119	30.5	.095	-1.02
22	.396	.357	.147	.115	.002	.106	25.2	.115	-0.94
23	.377	.267	.158	.125	.001	.109	23.2	.12	-0.92
24	.383	.285	.156	.12	.0022	.114	24.2	.12	-0.92
25	.30	.31	.185	.165	.0022	.106	17.5	.175	-0.76
26	.31	.211	.205	.205	.002	.111	14.1	.20	-0.70
27	.32	.22	.21	.225	.003	.104	13.0	.22	-0.66
28	.226	.347	.23	.25	.003	.078	11.6	.25	-0.60
29	.30	.18	.223	.25	.0025	.128	11.6	.25	-0.60
30	.218	.277	.233	.27	.003	.058	10.74	.27	-0.57
31	.131	.274	.265	.315	.001	.051	9.2	.31	-0.51
32	.134	.263	.321	.475	.014	.046	6.1	.47	-0.33

from experiments in silica crucibles in which neither the silicon nor the oxygen contents of the metal were particularly high. Values of f^0_{Si} have been obtained by dividing 2.9×10^{-3} by the values of $\frac{[\%Si].[\%O]^2}{(a_{SiO_2})}$ given in Table 11. Although a number of assumptions have been made in calculating f^0_{Si}, it is clear that many of the values are considerably below unity. Figure 41 shows the effect of oxygen percentage on f^0_{Si}. The MnO contents (expressed in mole fractions) for the individual points are shown in parenthesis. It is clear that there is no systematic deviation from the mean line which can be related to MnO content as was suggested by Schenck and Wiesner(29) and illustrated in Fig.10. A possible explanation of their results is that their low MnO contents (MnO < 10%) in silica-saturated slags correspond to high FeO contents and therefore high oxygen and low silicon contents in the metal. If the above hypothesis of an interaction between silicon and oxygen in molten iron is correct, K_{Si} values obtained from such experiments should be greater than those obtained with slags in which %MnO varied from 20-35. It might be expected that as the MnO content increased beyond some critical value, K_{Si} should begin to rise again when the position is reversed and the silicon contents are high and the oxygen contents low. It is interesting to note that, in spite of the scatter in the results of Korber and Oelsen(37) this trend is evident in their results at high MnO contents (40-45 percent) as can be seen in Fig.10(a). The results shown in Fig.41 have been replotted (Fig.42) to show the relationship between log f^0_{Si} and [%O], which can be expressed mathematically as,

$$\text{Log } f^0_{Si} = -7.5\,[\%O]$$

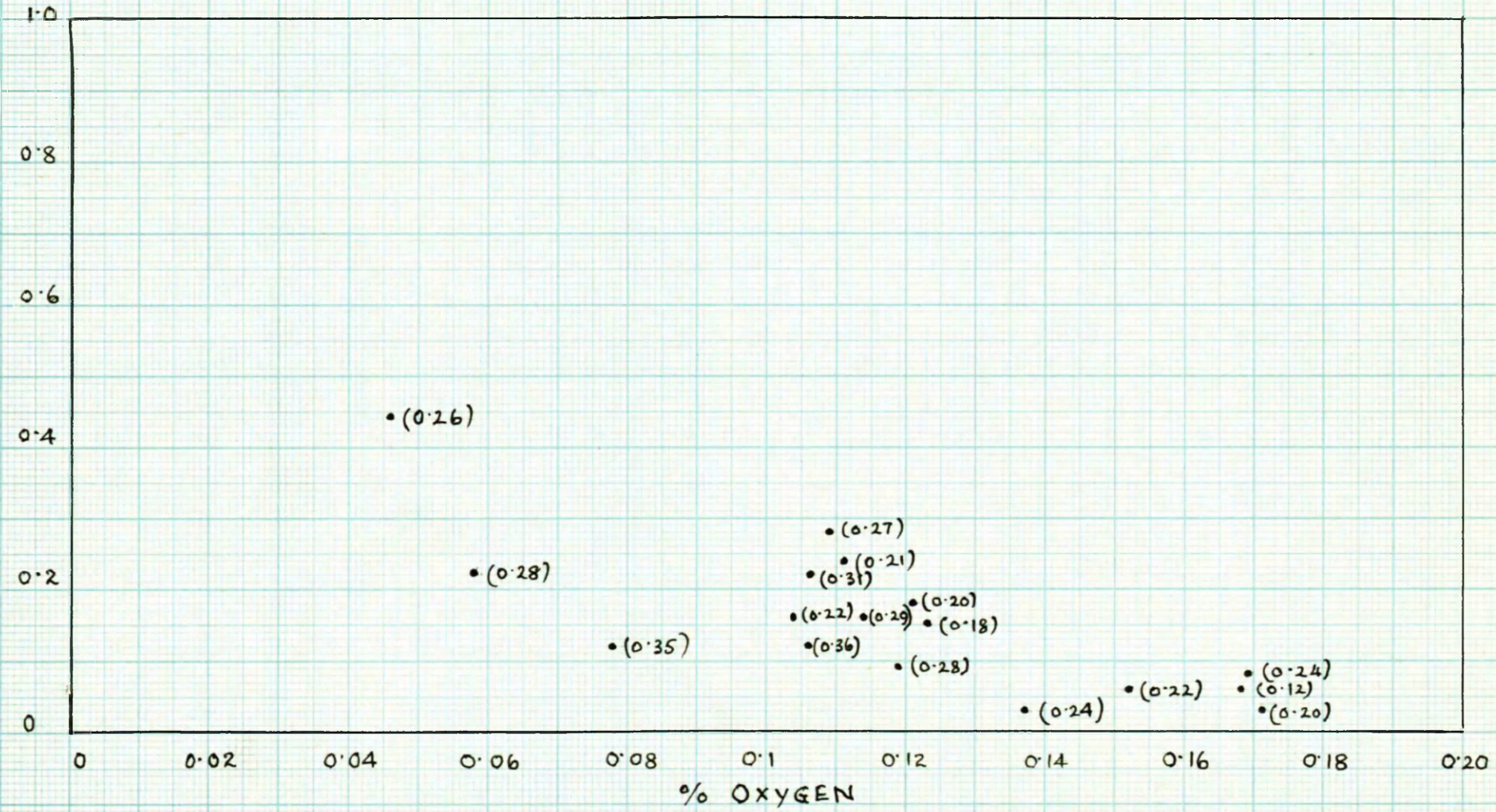


FIG.41. EFFECT OF OXYGEN ON ACTIVITY COEFFICIENT OF SILICON IN IRON.
(MnO CONTENT IN MOLE FRACTION IS SHOWN IN PARANTHESES)

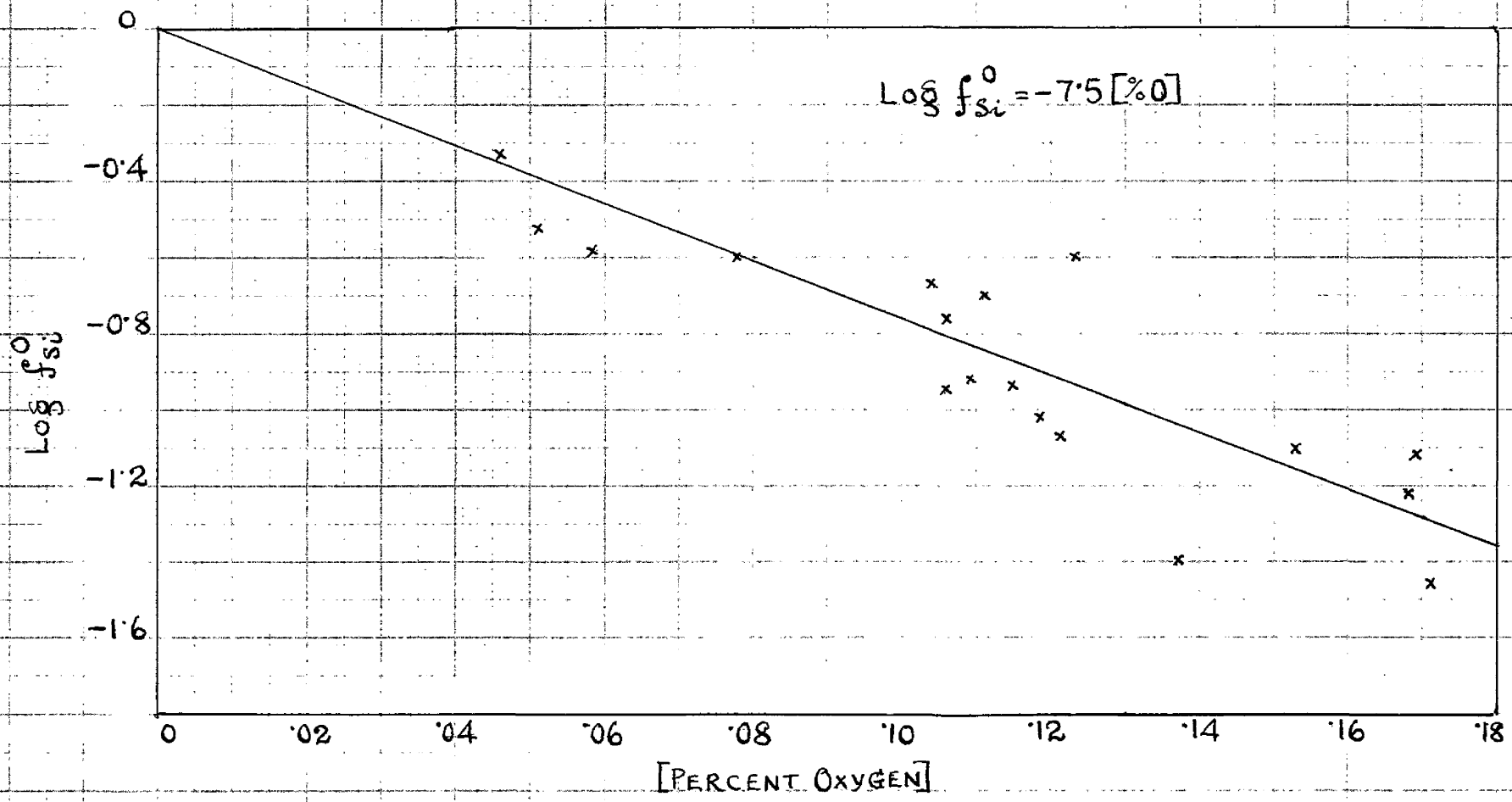


Fig. 42. Effect Of Oxygen On Activity Coefficient Of Silicon In Iron (1600°C)

$$\text{Ap} \quad \frac{\delta \log f_{Si}^{O}}{\delta [\%O]} = \frac{28}{16} \cdot \frac{\delta \log f_{O}^{Si}}{\delta [\%Si]}$$

$$\text{then} \quad \log f_{O}^{Si} = -\frac{7.5 \times 16}{28} \cdot [\%Si]$$

$$= -4.28 [\%Si]$$

It is clear from these equations that silicon and oxygen have a considerable effect on the activity of each other and that the assumption that the mean K'_{Si} value obtained from experiments in silica crucibles was a close approximation to the true K_{Si} value is not strictly valid. The method of successive approximations has therefore been used to recalculate both the true value of K_{Si} and values of $\log f_{Si}^{O}$ and $\log f_{O}^{Si}$, i.e., the above values for $\log f_{Si}^{O}$ and $\log f_{O}^{Si}$ have been applied to the slag-metal data obtained using silica crucibles to obtain a new value of K_{Si} which in turn is used to calculate new values of $\log f_{Si}^{O}$ and $\log f_{O}^{Si}$. This operation was repeated 6 times. The final values obtained were for 1600°C.

$$\frac{1}{K_{Si}} = 1.45 \times 10^{-3}$$

$$\log f_{Si}^{O} = -3.33 [\%O]$$

$$\log f_{O}^{Si} = -1.90 [\%Si]$$

These values for activity coefficients may be compared with the values

$$\log f_{Si}^{O} = -3.5 [\%O]$$

$$\log f_{O}^{Si} = -2.0 [\%Si]$$

which may be derived from the data of Gokcen and Chipman(31) for 1600°C.

Attention should, however, be drawn to the marked similarity between a_{SiO_2} and f^0_{Si} values given in Table 11. This suggests an alternative explanation for the apparent deviations of the values of

$$\frac{[\%Si][\%O]^2}{a_{SiO_2}}$$

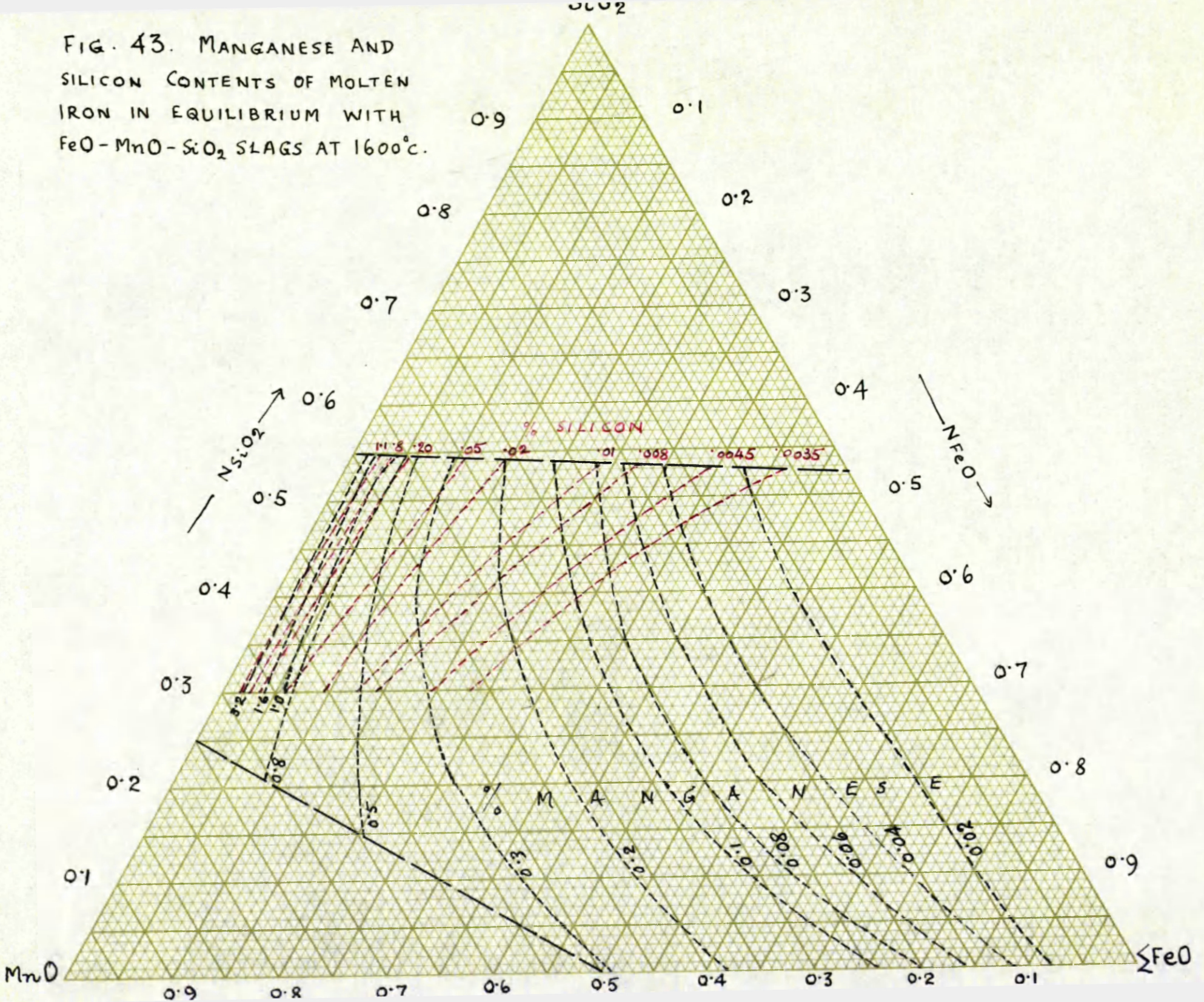
from that observed with silica saturated slags. Silica tubes were used to sample the molten metal, and if the reaction between silica and molten iron is extremely rapid, it is possible that within the 1-2 seconds during which sampling occurred, the metal was able to come into equilibrium with silica with respect to its silicon and oxygen content. The metal analyses recorded would then have been those in equilibrium with solid silica, i.e., $a_{SiO_2} = 1$, and it could then be deduced that within the limit of the present experimental errors silicon and oxygen did not affect each others' activity. Further work using sampling rods of a material other than silica would be necessary to elucidate this point.

(viii) Oxygen-Manganese - Silicon Equilibrium.

Fig.43 shows the manganese contents of molten iron in equilibrium with FeO-MnO-SiO_2 slags at 1600°C. This has been constructed by using the experimental points obtained at 1600°C together with the data of K'_{Mn} from Fig.34.

Lines of equal silicon contents are also shown in Fig.43. The values along the silica solubility curve were derived from the results of experiments in silica crucibles. Silicon contents in equilibrium with

FIG. 43. MANGANESE AND SILICON CONTENTS OF MOLTEN IRON IN EQUILIBRIUM WITH FeO - MnO - SiO_2 SLAGS AT 1600°C.



unsaturated silicates were calculated from the iso-activity curves for silica shown in Fig.39, the equilibrium oxygen contents given in Fig.28, and the value of 2.9×10^{-6} obtained for K'Si at 1600°C. These curves do not take into account a possible effect of oxygen on the activity of silicon for which a slight correction would be necessary. Such a correction would be greatest at high FeO contents and should not be appreciable over the range of compositions for which curves have been drawn.

If Fig.43 is used in conjunction with Fig.28, manganese, silicon and oxygen contents of molten iron in equilibrium with any given slag composition can be obtained.

Figs. 44 and 45 show the oxygen-silicon and oxygen-manganese relationship with varying amounts of manganese and silicon respectively. Data from Figures 27 and 43 have been used to obtain these relationships. The Mn-O and Si-O relationships obtained by Bell(16) at 1550°C are also shown in Figures 44 and 45.

From Fig.44, it becomes apparent that to obtain the same oxygen level at 1600°C, approximately 1.5 times the amount of manganese at a given silicon concentration will be required to obtain the same deoxidising effect as at 1550°C. This ratio increases as the manganese content and the level of deoxidation decrease.

Fig.45 shows the manganese-oxygen equilibrium at different silicon concentrations. The equilibrium content of oxygen is lowered slightly by manganese. The addition of very small amounts of silicon, e.g., 0.005% causes a substantial decrease in the oxygen content of the metal. An increase of temperature from 1550°C to 1600°C causes an appreciable

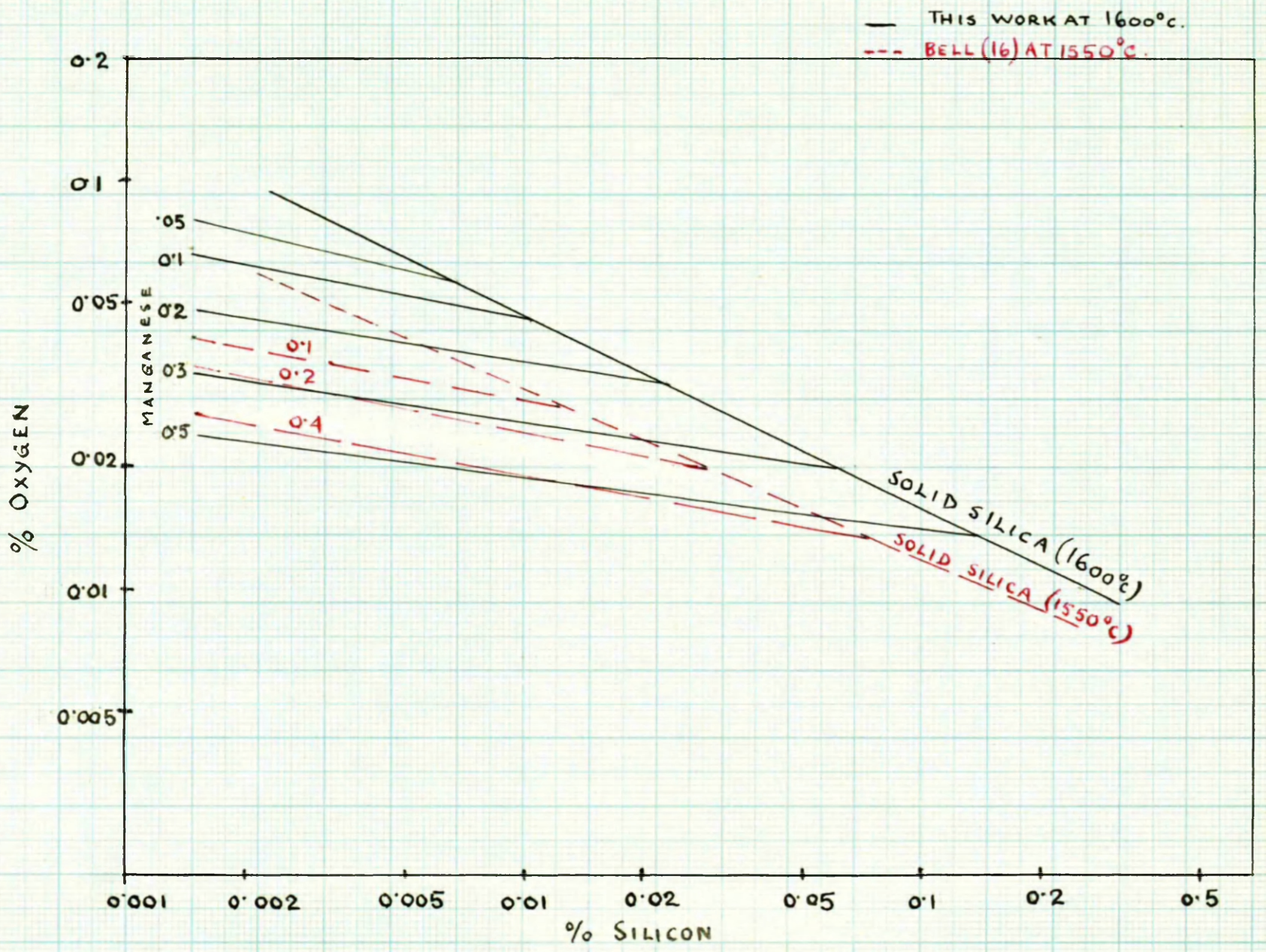


FIG. 44. EFFECT OF MANGANESE AND SILICON ON THE OXYGEN CONTENT OF MOLTEN IRON.

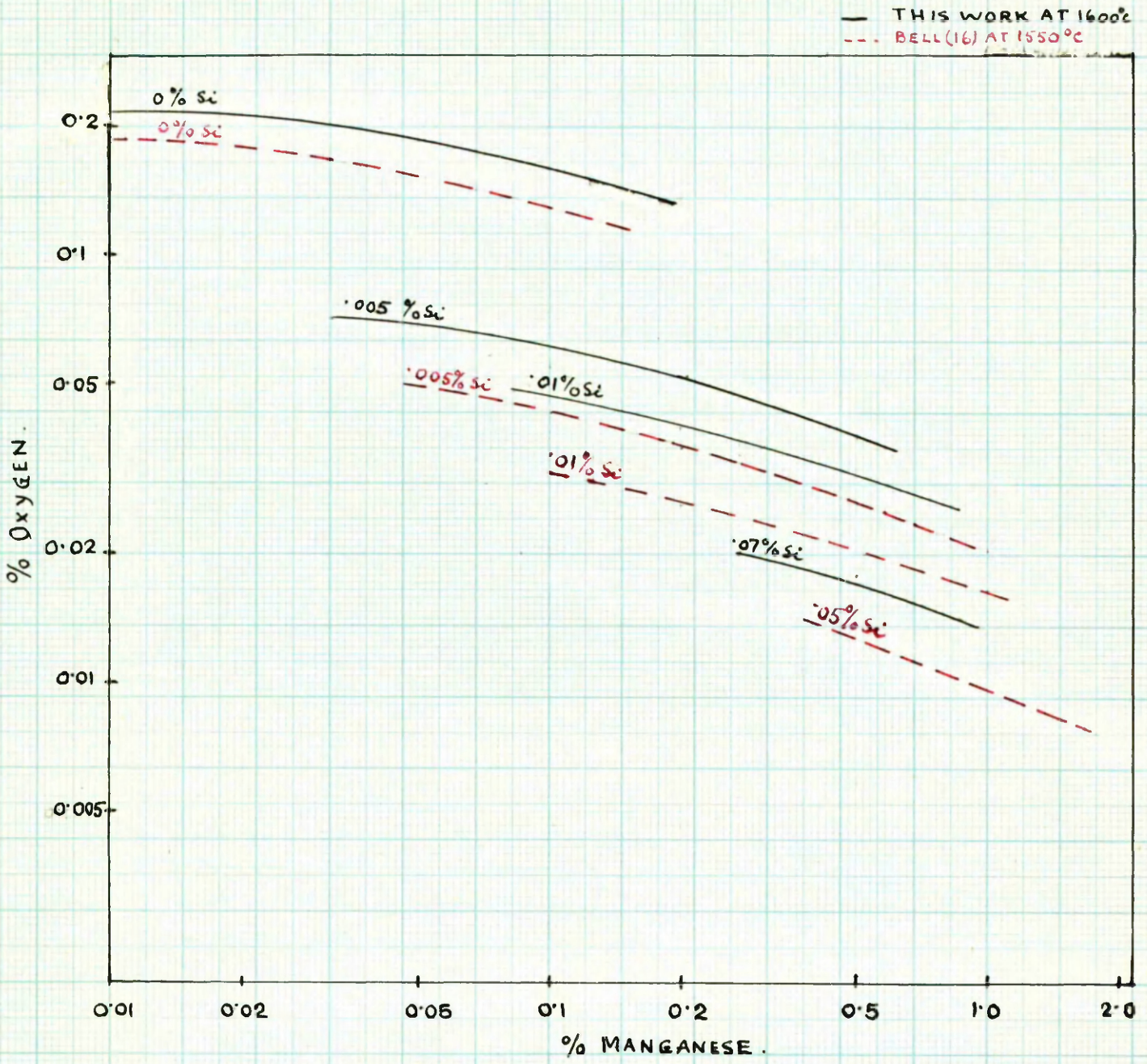


FIG. 45. MANGANESE - OXYGEN EQUILIBRIUM IN PRESENCE OF SILICON.

increase in oxygen content for similar manganese and silicon concentrations Thus at 0.1% manganese and 0.01% silicon, the oxygen contents at 1550°C and 1600°C are 0.033 and 0.045 percents respectively . Over the range of concentration shown in Fig.45, a fall in temperature from 1600°C to 1550°C causes a decrease in oxygen content of about 25-30 percent. The present results when compared with those of Hilty and Crafts(23) indicate that the reduction of oxygen solubility by manganese in the presence of silicon was not as high as was observed by the latter workers.

CHAPTER 8.

APPLICATIONS TO DEOXIDATION OF MOLTEN IRON.

APPLICATIONS TO DEOXIDATION OF MOLTEN IRON.

The object of deoxidation is to reduce to the desired level the amount of oxygen left in the molten metal after refining. It is usually regarded as preferable to use a deoxidiser or combination of deoxidisers which will not only meet the desired specification but which will also give rise to liquid deoxidation product. These are preferable to solid products because the suspended droplets of liquid can easily coalesce to form large inclusions which separate readily from the mass of the molten metal. Manganese-silicon alloys whose ratio is fixed by trial and error, are used in practice.

In this Chapter an attempt has been made to find out the degree of deoxidation that might be expected to take place after the addition of varying amounts of manganese-silicon deoxidisers. It is known from the work of Murad(48) that irrespective of FeO/MnO ratio low melting slags can be obtained near to 38-44 per cent SiO_2, the melting points being as low as 1200°C. Thus during deoxidation, if the manganese-silicon ratio is so adjusted that the compositions of the deoxidation products lie within this low-melting region, then at steel-making temperatures the deoxidation products will be highly superheated and very fluid, and should easily separate from the metal. An attempt has therefore been made to calculate the amount and composition of manganese-silicon deoxidiser that will be required to achieve any desired degree of deoxidation and at the same time produce such a deoxidation product.

For example, let us suppose that 100 gms. of iron containing 0.05% oxygen are to be deoxidised to give iron containing 0.005% oxygen, i.e., 90% of the oxygen is to be removed. Let it also be assumed

that a suitable deoxidation product would contain 0.4 mole fraction silica. It can bb seen from Fig.38 that an oxygen content of 0.005 percent would be in equilibrium with a slag of mole fraction $N_{FeO} = 0.023$ at 1600°C for $N_{SiO_2} = 0.4$. N_{MnO} is therefore 0.577. If the composition of the deoxidation product is converted into weight percentage, the following composition is obtained: $SiO_2 = 45\%$, $FeO = 1.5\%$ and $MnO = 53.5\%$. In the following calculation it will be assumed that iron does not contain any silicon and manganese before deoxidation.

Calculation.

Total Oxygen (Present when deoxidiser added). = [O] after deoxidation + oxygen in inclusion.

Mn(in deoxidiser) = [Mn] " " + manganese "

Si(in deoxidiser) = [Si] " " + silicon "

Let x = wt. of 'Mn' added in deoxidiser (grams).

" y = " " Si " " " "

" z = " " inclusion produced "

$$[Mn] = \frac{\gamma_{MnO}(\%MnO)}{K_{Mn}(\%FeO)} = A$$ (This can also be read off Fig.43).

and

$$[Si] = \frac{K_{Si}(a_{SiO_2})}{[O]^2} = B$$ (" " " " " " " " 43).

Oxygen Balance.

$$0.05 = (0.005) + z\left\{\left(\frac{\%SiO_2}{100} \times \frac{32}{60}\right) + \left(\frac{\%MnO}{100} \times \frac{16}{71}\right) + \left(\frac{\%FeO}{100} \times \frac{16}{72}\right)\right\}$$

Percentages of SiO_2, MnO and FeO are known.

Hence $z = 0.124$ gms.

Manganese Balance.

$$x = A + \left(z. \frac{\%MnO}{100} \times \frac{55}{71}\right)$$

Calculation or from Fig.43, $[Mn] = A = 1.92$

Hence $x = 1.97$.

Silicon Balance.

$$y = B + \left(z. \frac{\%SiO_2 \times 28}{100 \times 60}\right)$$

$B = [Si] = 0.8$ (Either by calculation or from Fig.43).

$y = 0.83$

∴ Weight of deoxidiser (assuming it only contains Mn + Si)

$= x + y = 1.97 + 0.83 = 2.80$ gms., i.e., 2.8%.

Ratio in Deoxidiser.

$$\frac{x}{y} = \frac{Mn}{Si} = \frac{1.97}{0.83} = 2.4 : 1.$$

This calculation has been repeated for different oxygen levels and for the removal of different percentages of oxygen. The results obtained are given in Table 12.

Since in steelmaking there is normally a small amount of residual manganese present at the end of the refining period, allowance should

TABLE 12.

[%] Removed	DEOXIDISER Weight Mn	Si	Mn+Si	Mn/Si Ratio	% Deoxidiser.	Composition of Inclusion. FeO%	MnO%	SiO_2%	Weight of Inclusions (grams)	Final Analysis of Steel. %Mn	%Si	%O	REMARKS.
Initial [O] = 0.20(1600°C).													
60	.16	.036	.25	2:1	.25	27	28	45	.335	.09	0.004	.08	
70	.21	.09	.30	2.3:1	.30	23	32	45	.357	.11	0.005	.06	
80	.42	.108	.53	3.8:1	.53	13	42	45	.44	.28	0.015	.04	
90	.72	.156	.88	4.5:1	.88	7.5	47.5	45	.50	.54	0.05	.02	
95	1.31	.31	1.62	4.2:1	1.62	3.5	51.5	45	.52	1.10	0.20	.01	
97.5	2.36	.93	3.29	2.5:1	3.29	1.5	53.5	45	.54	2.14	0.80	.005	
Initial [O] = 0.10(1600°C)													
60	.33	.047	.38	7:1	.38	13	42	45	.14	.28	0.015	.04	
70	.44	.061	.50	7:1	.50	10	45	45	.194	.37	0.023	.03	
80	.62	.098	.72	6.3:1	.72	7.5	47.5	45	.22	.54	0.05	.02	
90	1.20	.25	1.45	4.8:1	1.45	3.5	51.5	45	.247	1.1	0.20	.01	
95	2.03	.86	2.89	2.4:1	2.89	1.5	53.5	45	.26	1.92	0.80	.005	
Initial [O] = 0.05(1600°C)													
50	.45	.048	.49	9.3:1	.49	9	46	45	.07	.42	0.033	.025	
70	.79	.11	.90	7.1:1	.90	5	50	45	.097	.75	0.09	.015	
80	1.15	.22	1.37	5.1:1	1.37	3.5	51.5	45	.11	1.1	0.20	.01	
90	1.97	.83	2.80	2.4:1	2.80	1.5	53.5	45	.124	1.92	0.8	.005	
Initial [O] = 0.025(1600°C)													
50	.91	.137	1.05	6.7:1	1.05	4	51	45	.034	.90	.13	.0125	
60	1.12	.209	1.33	5.3:1	1.33	3.5	51.5	45	.041	1.1	.20	.01	
70	1.62	.37	1.99	4.4:1	1.99	2	53	45	.048	1.6	.36	.0075	
80	1.94	.81	2.75	2.4:1	2.75	1.5	53.5	45	.055	1.92	.80	.005	

TABLE 13.

Initial Mn = 0.2%) 1600°C
[O] = 0.20%)

% Removed	Deoxidiser Mn	Deoxidiser Si	Mn:Si Ratio	% Deoxidiser
70	0.01	0.09	1:9	0.10
80	0.22	0.107	2:1	0.33
90	0.524	0.156	3.36:1	0.68
95	0.91	0.31	2.93:1	1.26
97.5	2.16	0.93	2.3:1	3.09

Initial Mn = 0.2%) 1600°C
[O] = 0.1%)

60	0.129	0.047	2.75:1	0.18
70	0.24	0.063	4:1	0.30
80	0.42	0.098	4.3:1	0.52
90	1.00	0.252	4:1	1.25
95	1.83	0.855	2.1:1	2.69

Initial Mn = 0.2%) 1600°C
[O] = 0.05%)

50	0.245	0.048	5.1:1	0.29
70	0.587	0.11	5.3:1	0.70
80	0.945	0.223	4.24:1	1.17
90	1.77	0.828	2.1:1	2.6

Initial Mn = 0.2%) 1600°C
[O] =0.025%)

50	0.713	0.137	5.2:1	0.85
70	1.42	0.37	3.8:1	1.79
80	1.743	0.812	2.1:1	2.56

be made for this in the calculations. The data shown in Table 13 have been obtained in a similar manner to those of Table 12, but assuming that the molten metal contained 0.2 per cent residual manganese. It has also been assumed that the residual silicon content is negligible, which would be true at the end of refining in the basic open-hearth process but not in any acid process or after the reducing period of a basic electric process.

In Fig.46, the percentage weight of deoxidiser required to produce a fluid inclusion of the composition indicated above has been plotted against the percentage oxygen removed at different initial oxygen contents. Also shown are the final oxygen contents after deoxidation, as indicated by the dotted red lines. It would be seen:-

(a) As expected the percentage oxygen removed increases as the weight of deoxidiser added is increased. The increase in the amount of deoxidiser used increases rapidly beyond a certain percentage of oxygen removed which increases with the initial contents of the metal. As an example with an initial oxygen content 0.1%, the amount of deoxidiser required rises from 1.45 to 2.9 percent as the amount of oxygen removed is increased from 90 to 95 percent.

(b) The percentage of deoxidiser required increases as the initial oxygen content of the metal is decreased.

(c) The weight of deoxidiser required depends mainly on the final oxygen content and only increases slightly as the initial oxygen content is increased. Thus a final oxygen content of 0.02 percent can be

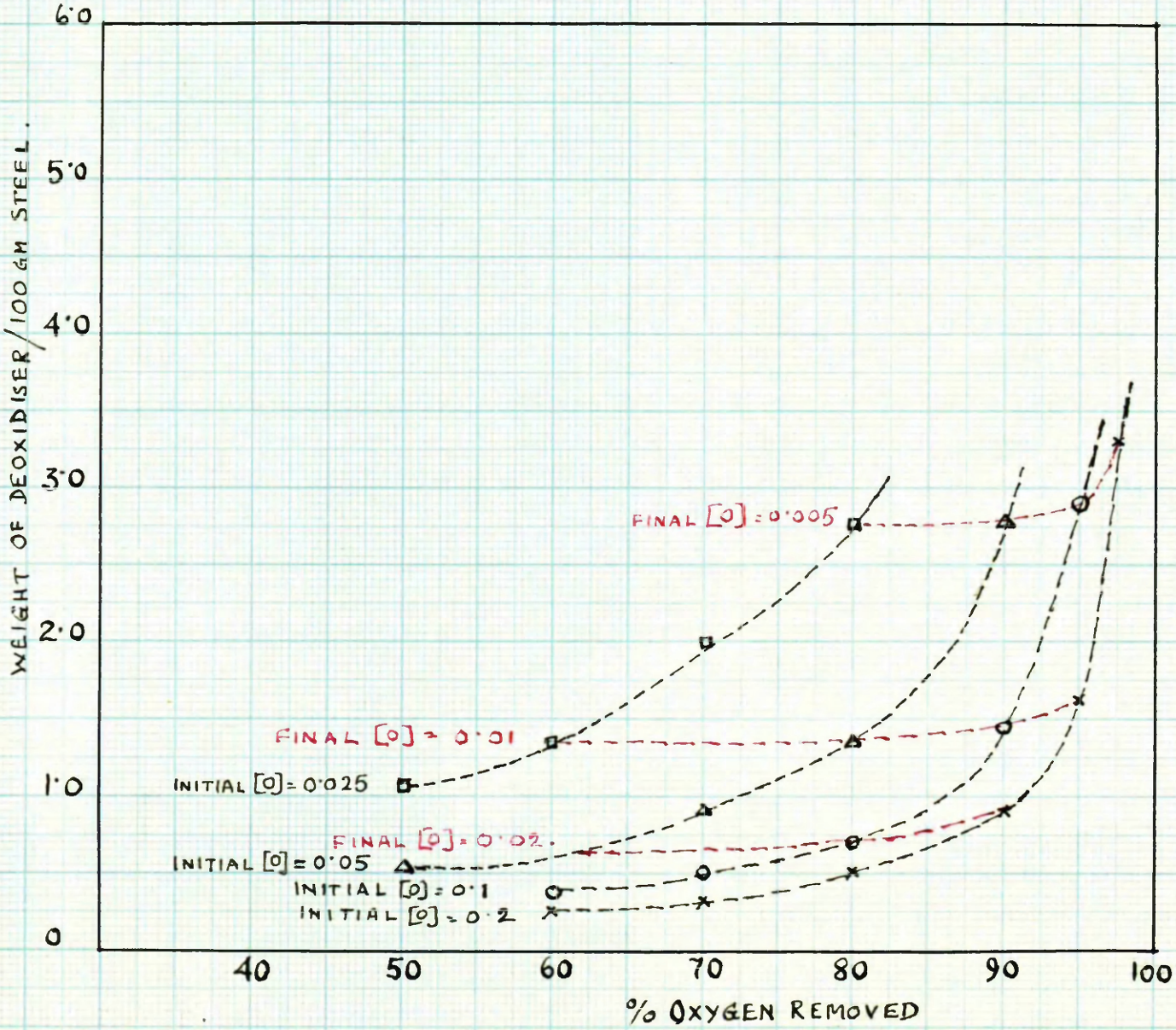


FIG. 46. RELATION BETWEEN AMOUNT OF DEOXIDISER ADDED AND PERCENTAGE OXYGEN REMOVED FROM MOLTEN IRON (1600°C)

achieved with additions of deoxidiser ranging from 0.7 to 0.85 percent of the iron weight for initial oxygen contents varying as much as 0.025 to 0.2 percent. This is also apparent from Fig.47 where the ~~initial~~ amount of deoxidiser used is plotted against final oxygen for different initial oxygen levels. This figure also indicates very clearly that the amount of deoxidiser required increases very rapidly for all initial oxygen levels as the final oxygen content decreases beyond 0.01 percent. It would be clearly uneconomical to carry out further deoxidation with manganese-silicon alloys beyond an oxygen level of about 0.01 percent and further deoxidation can be more economically obtained by the use of aluminium. It should be pointed out, however, that further deoxidation would be expected to take place as the temperature fell from 1600°C to the freezing point of iron and the final oxygen levels quoted above can be regarded as about 20 percent higher than those which may be reasonably expected in practical works deoxidation. The figure of 20 percent is derived from a comparison of oxygen level obtained in the present work with those obtained by Bell(16) for similar slag composition at 1550°C.

Fig.48(a) and (b) show the relationship between the final oxygen content of molten iron at 1600°C and the manganese-silicon ratio of the deoxidiser required to form liquid deoxidation products without and with manganese initially present in the molten iron. The latter case is more rpresentative of practical deoxidation since residual manganese contents of 0.15 to 0.25 percent are commonly met in practice. It can be seen that no single manganese-silicon ratio of deoxidiser is suitable

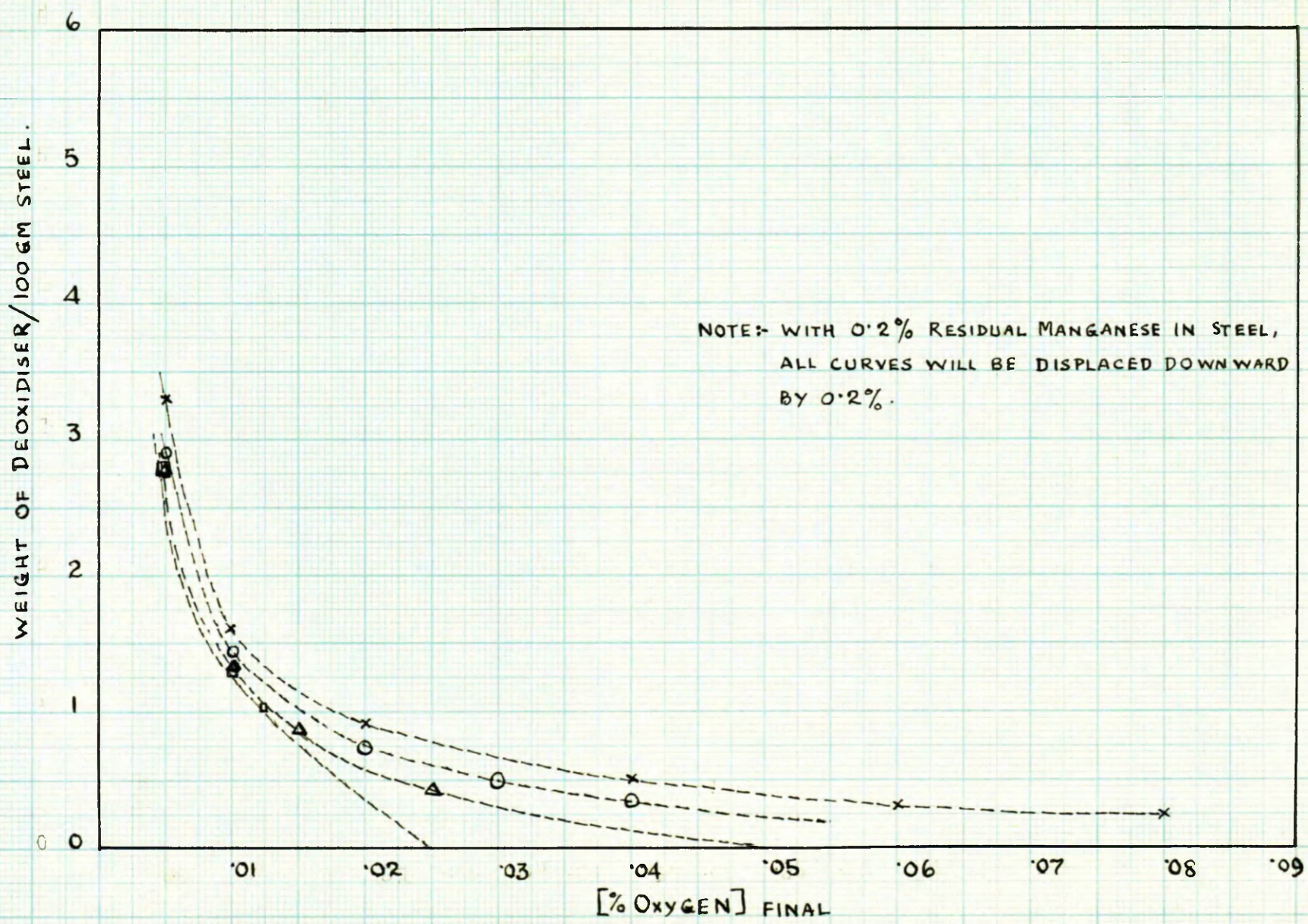


FIG. 47. RELATION BETWEEN FINAL OXYGEN CONTENT OF MOLTEN IRON AT 1600°C AND AMOUNT OF DEOXIDISER ADDED.

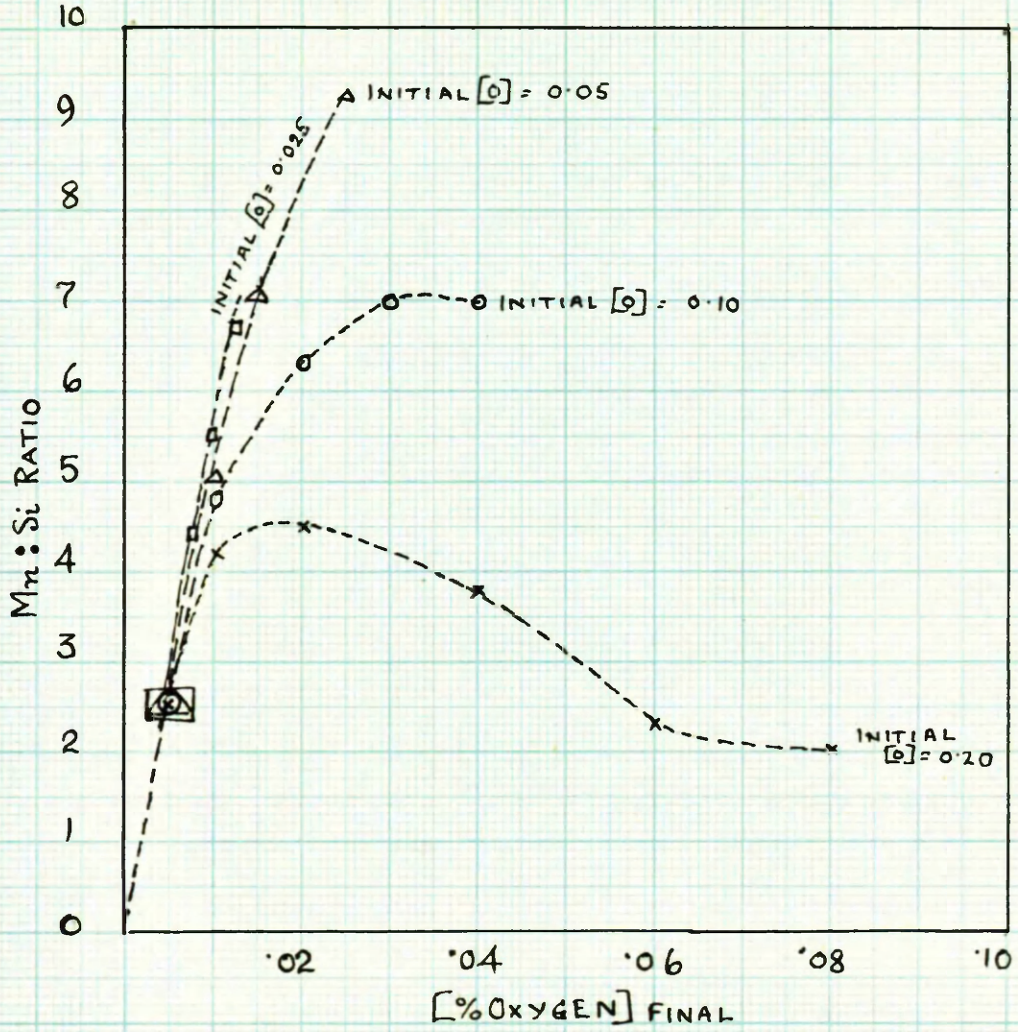


FIG. 48(a). RELATION BETWEEN FINAL OXYGEN CONTENT OF MOLTEN IRON AT 1600°C AND Mn/Si RATIO IN DEOXIDISER REQUIRED TO PRODUCE FLUID INCLUSIONS (NO MANGANESE PRESENT INITIALLY).

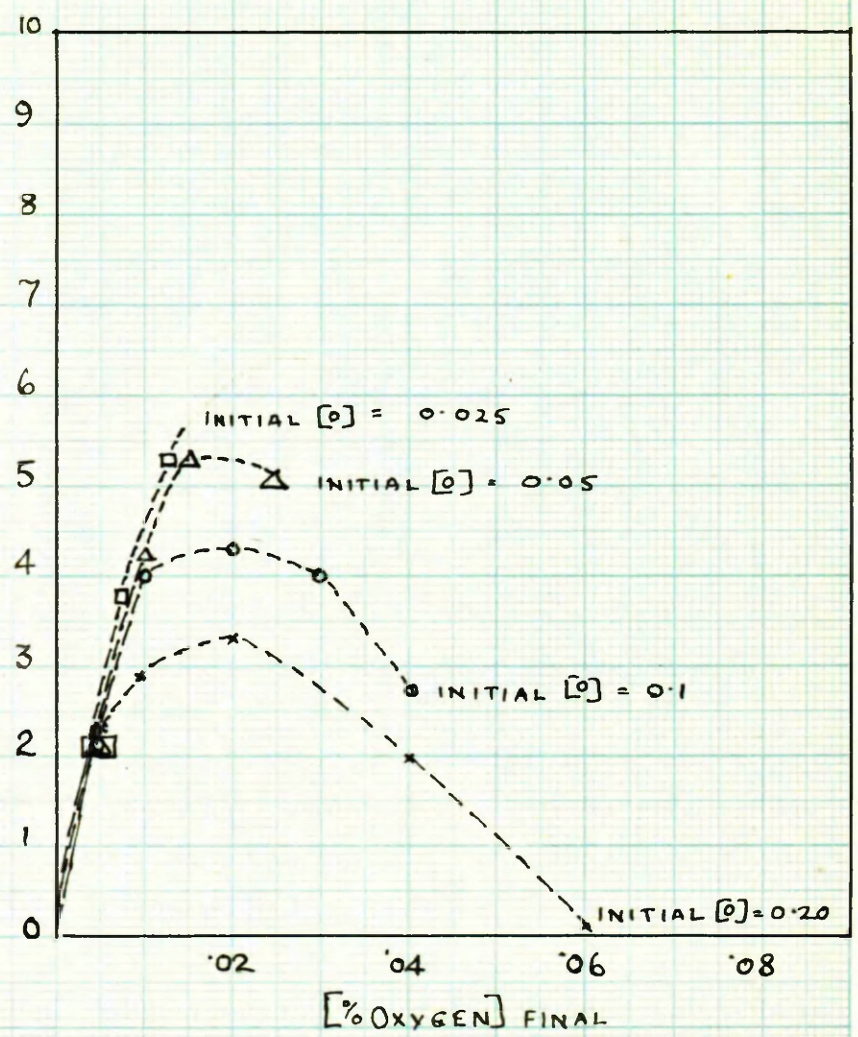


FIG. 48(b). RELATION BETWEEN FINAL OXYGEN CONTENT OF MOLTEN IRON AT 1600°C AND Mn/Si RATIO IN DEOXIDISER REQUIRED TO PRODUCE FLUID INCLUSIONS (0·2% MANGANESE PRESENT INITIALLY).

in all cases and that for each initial oxygen level, the manganese-silicon ratio appears to reach a maximum. Oxygen contents at the end of refining in the open-hearth furnace would be expected to lie well within the limit 0.025 to 0.1 percent. It has already been indicated that uneconomical amounts of deoxidiser would be required if oxygen levels much below 0.01 percent were desired. Assuming a residual manganese content of 0.2 percent, it would be seen from Fig.48(b) that the requisite manganese-silicon ratio in the deoxidiser lies between the limit of about 3.5 to 4.5 which is typical of manganese-silicon deoxidisers in present day use. Fig.48(b) shows also that the optimum manganese-silicon ratio decreases rapidly as the degree of deoxidation required increases. This would naturally correspond to rapid increase in the residual silicon content in the deoxidised metal.

LABORATORY DEOXIDATION EXPERIMENTS.

It was mentioned under the heading of "Experimental Technique" that at the conclusion of some of the slag-metal experiments, manganese-silicon deoxidiser was added. Further metal samples were taken after allowing the melt to stand for times varying from 1 to 15 minutes. The results obtained from these experiments are shown in Table 14. In several experimental runs more than one deoxidised sample was taken after the addition of deoxidiser at different times. This is indicated by I or II after the melt number, as shown in Column 2. Deoxidisers with Mn:Si ratios of 4:1 and 5:1 were used, as it had been shown from the earlier experiments that such deoxidisers would be expected to

TABLE 14.

Results on Deoxidation by Mn-Si Alloy.

Temp. °C.	Melt No.	Before Deoxidation %Mn	%Si	%O	Wt. of Metal deoxidised.	Wt. of deoxidiser added (gms)	Ratio of deoxidiser	Time allowed before sampling	After Deoxidation %Mn	%Si	%O
1600	D1(d)I	0.045	<0.001	0.168	49 gms.	0.51	5:1	1 min.	0.274	0.0255	0.026
"	D1(e)I	0.060	0.0015	0.148	43.5 "	0.45	5:1	4 "	0.202	0.0045	0.116
"	D1(e)II	0.060	0.0015	0.148			5:1	15 "	0.097	0.006	0.141
"	D3(a)I	0.078	<0.001	0.16	45 "	0.51	5:1	1 "	0.268	0.01	0.086
"	D3(a)II	0.078	<0.001	0.16			5:1	5 "	0.32	0.049	0.102
"	D23(I)	0.045	<0.001	0.168	32 "	0.49	5:1	3 "	0.148	0.008	0.097
"	D13(I)	0.084	0.026	0.038	55 "	0.50	5:1	4 "	0.342	0.08	0.023
"	D14(II)	0.07	0.013	0.046	63 "	0.49	5:1	6 "	0.348	0.043	0.0296
"	D29(I)	0.083	0.002	0.111	44 "	0.51	4:1	7 "	0.22	0.004	0.0636
"	D31(I)	0.072	0.0025	0.123	24 "	0.51	4:1	10 "	0.30	0.0018	0.0643
"	D15(I)	0.048	0.0075	0.062	51 "	0.53	5:1	5 "	0.279	0.05	0.0406
"	D35(I)	0.135	0.0022	0.114	28 "	0.52	4:1	8 "	0.394	0.0036	0.040

give liquid deoxidation product when added in amounts of about 1%, particularly at high initial oxygen contents.

It will be seen from Table 14 that the oxygen contents after deoxidation are greater than those indicated by Fig.47. Thus, using 1% deoxidiser, the highest oxygen content expected would be 0.018% even when the iron was initially saturated with oxygen. In Fig.49 the final oxygen content after deoxidation is plotted against time elapsed after addition of deoxidiser, the initial conditions being approximately the same, viz., oxygen content of metal = 0.15 - 0.17%, percentage deoxidiser used about 1, and Mn/Si ratio of deoxidiser, 5.1. It is clear that the oxygen content rises after addition of deoxidiser towards the oxygen content which was initially present and in equilibrium with the overlying slag. The oxygen content rises due to transfer of oxygen from slag to metal. This process occurs rapidly during the first two minutes after deoxidation. The number of results at other oxygen levels where the deoxidation conditions are similar are insufficient to give a curve of the type as shown in Fig.49, but a similar trend is shown by them.

The rapid increase in oxygen content after deoxidation in the present work is mainly due to the small quantities of metal and slag present. In practical deoxidation, an increase in oxygen content after deoxidation would be expected to occur but not to the same degree due to the larger depths of metal and slag. Further factors limiting the reversal of oxygen from slag to metal are the fall in temperature which normally occurs during deoxidation, particularly in the ladle and the removal of most of the slag which occurs before ladle deoxidation.

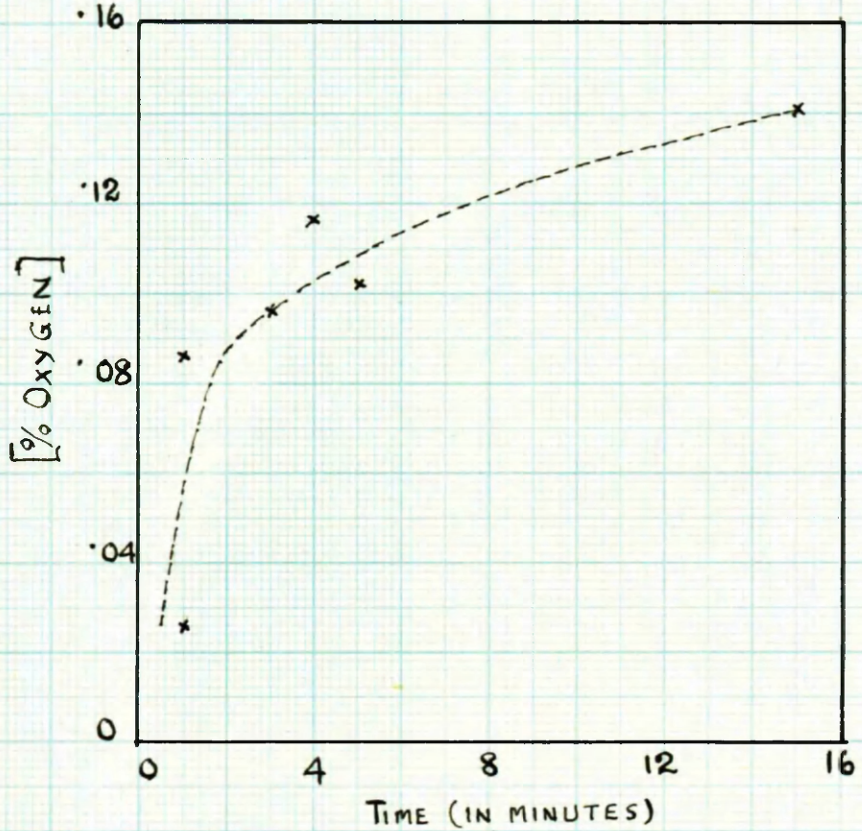


FIG. 49. INCREASE OF OXYGEN CONTENT OF MOLTEN IRON WITH TIME AFTER ADDITION OF DEOXIDISER.

It was not possible in the present experiments to remove the slag completely before deoxidation, but it is believed that oxygen contents approaching the theoretical values would have been attained in the absence of the slag.

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